



Deep Fork River Water Quality Study

Final Summary Report – March 2019



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Oklahoma Ecological Services Field Office

In cooperation with:

- Deep Fork National Wildlife Refuge
- National Wildlife Refuge System, Region 2, Inventory and Monitoring Program
- National Wildlife Refuge System, Region 2, Division of Water Resources
- Oklahoma Department of Wildlife Conservation
- Oklahoma Department of Environmental Quality State Environmental Laboratory Services Division

Front Cover: Deep Fork River within the Deep Fork National Wildlife Refuge, Okmulgee, OK

Photo Credit: USFWS (November 17, 2014)

Introduction

In 2014, the US Fish & Wildlife Service (Service) initiated a water quality study in the Deep Fork River (river) in the vicinity of the Deep Fork National Wildlife Refuge (refuge) near Okmulgee, OK. This project was a cooperative effort involving personnel from the Oklahoma Ecological Services Field Office, the refuge, the National Wildlife Refuge System Inventory and Monitoring Program (I&M) and the National Wildlife Refuge System (NWRS) Division of Water Resources (DWR). The primary project partner was the Oklahoma Department of Wildlife Conservation (ODWC). Laboratory analyses were performed by the Oklahoma Department of Environmental Quality's (ODEQ) State Environmental Laboratory Services Division.

The goal of this study was to gather and evaluate water quality information on the river in reaches that flow through the refuge. Information collected during this project will be used to determine the current water quality conditions in the river and may be used to support management decisions regarding the important natural resources protected within the refuge.

Study Sites

The refuge was established in 1993 to protect the bottomland hardwood forests and related ecosystems along the banks and floodplain of the river. Currently, the refuge protects over 10,000 acres and 34 river miles. This study was designed to provide baseline water quality information for the river across two separate calendar years.

Table 1. Site names, geographic location, and river distance between sample sites.

Site Name	Latitude	Longitude	River Distance to Next Site (km)
Okmulgee Wildlife Management Area	35.65685°	-96.03633°	11.90
Downstream of CP Kelco Discharge	35.60623°	-96.00965°	9.98
Upstream of Okmulgee Creek	35.58742°	-95.99335°	1.75
Budweiser Tract	35.58037°	-95.98430°	27.00
Coalton Bridge	35.50410°	-95.92340°	-

Four sampling sites were selected based on known contaminant inputs to the river plus a reference site upstream on the Okmulgee Wildlife Management Area (WMA) (Figure 1). These sites are listed in Table 1. This study comprised 27 sets of monthly and three low discharge water quality samples. Figure 2 indicates the sample collection dates and discharge at the time of collection, which began in August 2014 and continued until March 2017. Sampling occurred mid-month during the collection periods, but sampling delays occurred when field conditions prevented safe river access.

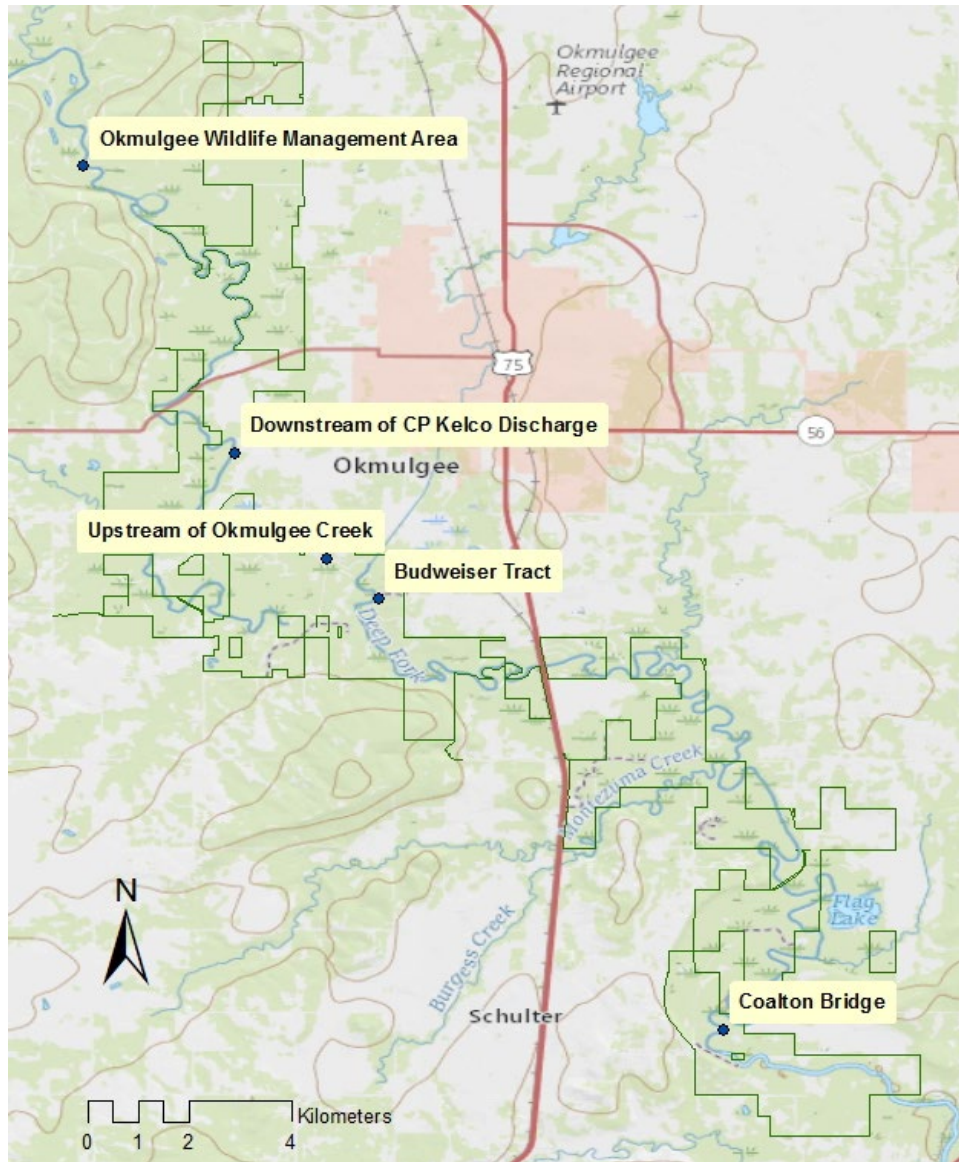


Figure 1. Deep Fork River Water Quality Study Sample Location Map. Sample sites (blue dots) are labeled with site names. The Deep Fork National Wildlife Refuge is outlined in green.

Methods

Sampling

The field parameters listed in Table 2 were measured using a Hydrolab® or other similar handheld water quality meter. The remaining analytes were measured by the Oklahoma Department of Environmental Quality's (ODEQ) State Environmental Laboratory Services Division using methods specified in Table 2. Sampling occurred during two intervals each of which lasted at least one-calendar-year: August 2014 through October 2015 and April 2016 through March 2017. Total dissolved solids, oil and grease, and total petroleum hydrocarbons (including diesel, gasoline, and lube oil range organics) were added to the analyte list for the second sampling interval. Generally, samples were taken on a day between the 14th

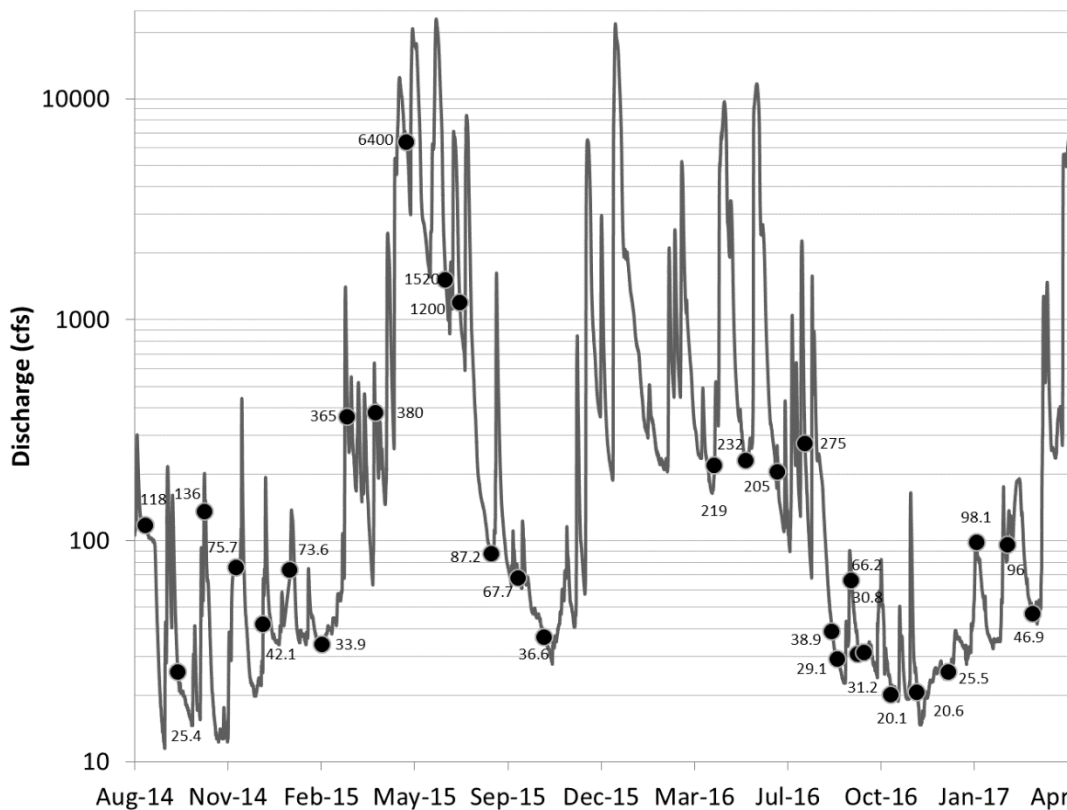


Figure 2. Deep Fork River discharge (cubic feet per second, gray line, from USGS stream gauge) with sampling times indicated (solid black circles) by date (month and year). The discharge at each sampling event is labeled near the black circle representing each sampling event.

and 20th of each sampled month, but specific sample dates can be found in the raw data hosted at the Open Science Framework (https://osf.io/pwys6/?view_only=44953db8df0e41be881264ebc4930528). Discharge measurements were downloaded from the US Geological Survey (USGS) stream gauge located on the Deep Fork River near Beggs, OK (station ID 07243500).

Sample Collection: Samples were collected using a grab sampling technique and then placed into a churn splitter. Samples were collected by extending a clean 1 liter (L) bottle on a pole out into the river just under the surface of the water and allowing the river water to fill it. Grab samples were taken until the churn splitter was filled. Churning of the sample was done at a slow, consistent pace. The churn splitter was then used to aliquot a composite sample into various bottles for analysis. The spigot was kept free of obstructions so that a continuous, even flow exited the bucket into the sample containers (provided by the analytical laboratory). Samples for hydrocarbon analyses (analytes for methods EPA 1664B and TNRCC 1005M) were collected in glass bottles or vials directly from the river and not the churn splitter.

During each sampling event, at least one duplicate or split sample was collected to control for the sample splitting method. The duplicate sample helped ensure that composite samples were being collected appropriately. As described above, duplicate samples were collected by using a churn splitter to divide water from one sample site into two separate samples. The label for the split sample was given the sample number “6”. Notes were made in the “Other Comments” section on the Data Collection form

indicating that a duplicate sample was collected. Analysis of the split samples can be found in Appendix B.

Table 2. Units, location of measurement, and method used to measure water quality parameters.

Analyte	Units	Location	Method
pH	None	Field	Handheld Water Quality Meter
Dissolved Oxygen	mg/L	Field	Handheld Water Quality Meter
Oxygen Saturation	% Saturation	Field	Handheld Water Quality Meter
Oxygen Reduction Potential (ORP)	mV	Field	Handheld Water Quality Meter
Specific Conductivity	µS/cm	Field	Handheld Water Quality Meter
Water Temperature	°C	Field	Handheld Water Quality Meter
Total Alkalinity	mg/L as CaCO ₃	Laboratory	EPA 310.2
Chloride	mg/L	Laboratory	EPA 325.2
Sulfate	mg/L	Laboratory	EPA 375.4
Total Dissolved Solids	mg/L	Laboratory	SM2540C
Ammonia	mg/L	Laboratory	EPA 350.1
Nitrate + Nitrite	mg/L as N	Laboratory	EPA 353.2
Total Kjeldahl Nitrogen	mg/L	Laboratory	EPA 351.2
Total Phosphorus	mg/L	Laboratory	EPA 365.3
Total Hardness	mg/L	Laboratory	EPA 130.1
True Color	Pt/Co	Laboratory	EPA 110.2
Total Cyanide	mg/L	Laboratory	EPA 335.4
Dissolved Potassium	mg/L	Laboratory	EPA 200.7
Total Potassium	mg/L	Laboratory	EPA 200.7
Total Chromium	µg/L	Laboratory	EPA 200.8
Total Copper	µg/L	Laboratory	EPA 200.8
Dissolved Iron	µg/L	Laboratory	EPA 200.7
Total Lead	µg/L	Laboratory	EPA 200.8
Dissolved Aluminum	µg/L	Laboratory	EPA 200.8
Oil and Grease	mg/L	Laboratory	EPA 1664B
Diesel Range Organics	mg/L	Laboratory	TNRCC 1005M
Gasoline Range Organics	mg/L	Laboratory	TNRCC 1005M
Lube Oil Range Organics	mg/L	Laboratory	TNRCC 1005M
Total Petroleum Hydrocarbons	mg/L	Laboratory	TNRCC 1005M

Sample Preservation: After each sample was split into the collection bottles, sulfuric acid (H₂SO₄) was added to one bottle for preservation and 1:1 hydrochloric acid (HCl) to the glass bottles (oil and grease analysis), upon returning to the vehicle. Before sampling, the ODEQ added sodium hydroxide (NaOH) to one of the bottles and HCl to the glass vials (total petroleum hydrocarbons analysis) for each site. Each container was labeled by ODEQ for identification. Other bottles did not receive acid or other preservative. All samples were stored on ice and delivered to the analytical laboratory within 24 hours of sampling.

Decontamination of sampling equipment: The churn splitter and grab sampler were cleaned with Alconox™ at each site before sampling began. The Hydrolab® was rinsed with site water and was allowed to equilibrate at the site for at least five (5) minutes before readings were recorded.

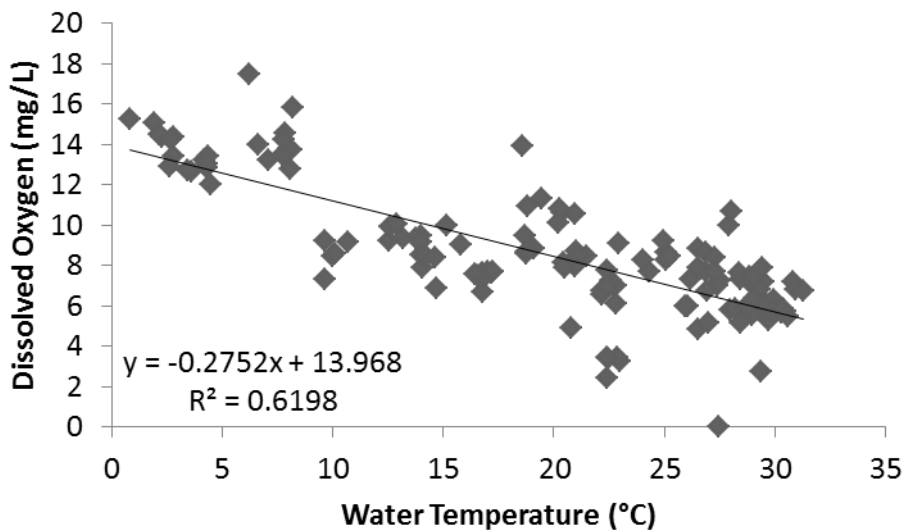
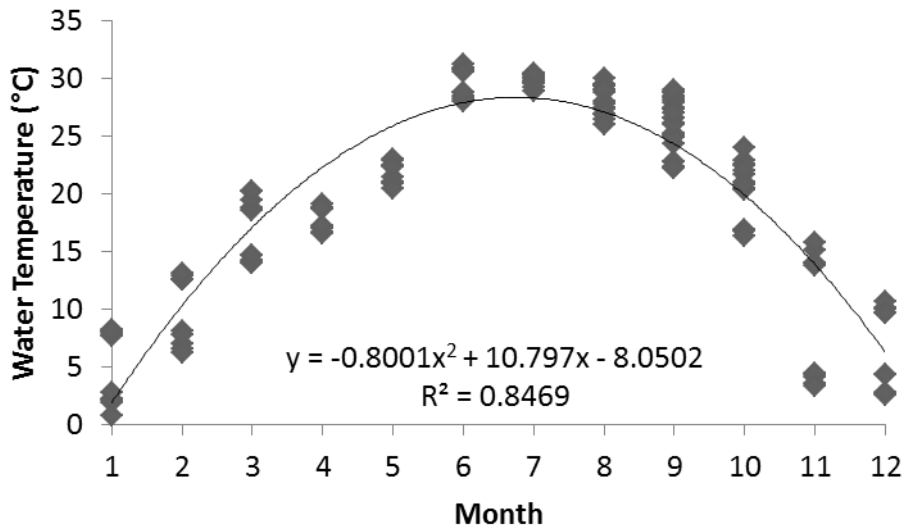


Figure 3. Plots of the seasonally dependent variables water temperature (top, plotted versus month) and dissolved oxygen (bottom, plotted versus water temperature). Regressions and fit statistics are given for each seasonal relationship.

Data Analysis

Data management, summary statistics, graphs, and univariate statistics were calculated in Microsoft Excel (Redmond, WA). Maps or other georeferenced analyses were generated using ESRI ArcMap (Redlands, CA). Principal Components Analysis (PCA) and multiple linear regressions of water quality variables was completed using R (version 3.3.2, R Core Team 2017).

Results and Discussion

Measured water quality parameters covered under Oklahoma water quality standards (Oklahoma Administrative Code, Title 785, Chapter 45) were dissolved oxygen, total chromium, total copper, and total lead. Overall (Table 3) and site by site (Table 4) mean values for those parameters were at levels protective of the Deep Fork River's designated use and propagation of warm water aquatic communities (the designated use of the Deep Fork of the Canadian River downstream of Arcadia Lake). The exception was 25, or 17%, of the dissolved oxygen measurements were below 6.0 milligram per liter (mg/L), which Oklahoma water quality standards list as protective of the early life stages of warm water aquatic communities. However, only nine measurements, or 6% of measurements, fell below 5.0 mg/L dissolved oxygen, which is protective of other life stages of warm water aquatic communities. Additionally, no measured parameters exceeded numerical criteria to protect beneficial uses, as listed in Oklahoma water quality standards.

Water temperatures and pH were normal compared to historic averages for the region (USGS 1977). Total alkalinity, chloride, nitrate + nitrite as N, total Kjeldahl nitrogen (TKN), and total phosphorus all averaged above the national average, with total phosphorus exceeding the national average by over two times. Total hardness, a measure of divalent cations, was greater than the national average and would be classified as very hard (USGS 1977). Sulfate and total dissolved solids were below the national average. Ammonia, total cyanide, oil and grease, diesel range organics, gasoline range organics, lube oil range organics, and by extension total petroleum hydrocarbons (this parameter is the sum of the three previous parameters) were not detected or not detected frequently enough to reliably draw conclusions.

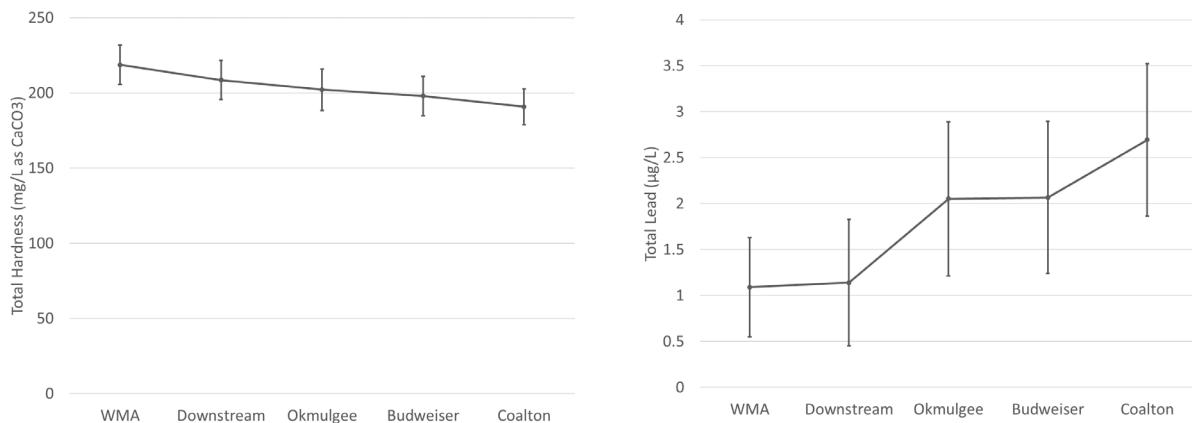


Figure 4. Water quality parameters that changed with the river gradient. Total hardness (left graph) decreased while total lead (right graph) increased from the upstream to downstream sites. Error bars are standard error of the mean.

Table 3. Summary statistics for measured water quality parameters across all sites and sampling events. (parameter units are given in Table 2)

Analyte	Mean	Standard Deviation	Maximum	Minimum
pH	7.74	0.57	9.10	5.81
Dissolved Oxygen	8.57	3.08	17.50	0.02
Oxygen Saturation	89.6	22.3	149.1	0.3
Specific Conductivity	713.1	311.8	1638.0	149.9
Water Temperature	19.94	8.78	31.28	0.84
Total Alkalinity	168.4	67.1	297.0	0.0
Chloride	108.3	55.1	228.0	12.5
Sulfate	59.0	17.6	113.0	34.1
Total Dissolved Solids	468	122	706	144
Ammonia	0.00	0.03	0.20	0.00
Nitrate + Nitrite	0.73	1.57	17.00	0.00
Total Kjeldahl Nitrogen	1.16	0.32	2.35	0.56
Total Phosphorus	0.674	1.219	13.300	0.039
Total Hardness	203.6	70.8	322.0	69.4
True Color	191	236	1130	12
Total Cyanide	0.000	0.001	0.011	0.000
Dissolved Potassium	7.65	3.93	21.50	2.96
Total Potassium	8.75	3.66	21.50	3.54
Total Chromium	2.94	4.84	18.80	0.00
Total Copper	2.06	4.24	35.80	0.00
Dissolved Iron	156.4	211.2	951.0	0.0
Total Lead	1.81	4.12	19.20	0.00
Dissolved Aluminum	79	144	740	0
Oil and Grease	0.4	1.6	7.9	0.0
Diesel Range Organics	0.00	0.00	0.00	0.00
Gasoline Range Organics	0.00	0.00	0.00	0.00
Lube Oil Range Organics	0.00	0.00	0.00	0.00
Total Petroleum Hydrocarbons	0.00	0.00	0.00	0.00

Trends between sites or sample dates was explained for most variables by the natural gradients of seasonality, physical/chemical relationships, stream gradient, and discharge volume. Water temperatures varied with seasons and were hottest during July (summer) and coldest during January (winter, Figure 3). The Ideal Gas Law ($PV=nRT$ or $n=PV/RT$) states that for a given pressure and volume (i.e., one liter of water in Okmulgee, OK), the number of moles present of a gas is inversely proportional to temperature. On average, this relationship allows water temperature to explain 62% of the variability in measured dissolved oxygen concentrations during the study (Figure 3). Total hardness decreased while total lead increased from upstream to downstream during the study (Figure 4). The changes in concentration from upstream to downstream sites indicates that tributaries of the Deep Fork River have

Table 4. Sample size (N), mean, and standard deviation (SD) for water quality parameter by sample site across sampling events. (parameter units are given in Table 2)

	N	WMA		Downstream		Okmulgee		Budweiser		Coalton	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH	30	7.85	0.49	7.84	0.47	7.80	0.53	7.76	0.58	7.44	0.67
Dissolved Oxygen	30	8.39	3.30	8.62	2.95	8.87	2.85	8.98	2.89	8.07	3.48
Oxygen Saturation	30	87.3	19.7	92.0	18.0	91.0	25.1	93.5	18.1	84.7	28.1
Specific Conductivity	29	724.8	304.5	813.0	337.4	711.6	319.1	672.6	312.1	642.2	277.5
Water Temperature	30	19.68	9.05	20.48	8.87	19.82	8.92	19.93	8.84	19.77	8.80
Total Alkalinity	30	173.2	61.6	181.4	70.2	168.7	69.3	164.5	65.7	153.9	69.9
Chloride	30	111.8	54.5	115.0	57.7	110.7	58.7	107.2	55.7	96.9	50.6
Sulfate	30	60.3	14.1	59.1	16.5	58.6	19.8	56.9	18.7	60.2	19.3
Total Dissolved Solids	15	461	117	493	136	486	131	464	123	435	111
Ammonia	30	0.01	0.04	0.01	0.03	0.00	0.02	0.00	0.02	0.00	0.02
Nitrate + Nitrite	30	0.55	1.09	0.80	0.78	1.06	3.10	0.82	0.77	0.41	0.59
Total Kjeldahl Nitrogen	30	1.02	0.32	1.17	0.35	1.12	0.27	1.24	0.29	1.25	0.34
Total Phosphorus	30	0.212	0.134	0.977	1.062	0.592	0.463	0.689	0.492	0.898	2.380
Total Hardness	30	218.7	72.5	208.5	71.0	202.1	75.5	197.9	71.1	190.8	65.2
True Color	30	169	182	198	240	207	269	192	265	191	228
Total Cyanide	30	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
Dissolved Potassium	30	4.67	1.01	10.29	5.61	7.97	3.34	7.91	3.04	7.43	3.12
Total Potassium	30	5.72	1.08	11.27	5.25	9.15	2.98	9.02	2.72	8.60	2.70
Total Chromium	30	2.75	4.21	2.48	4.32	2.91	4.83	2.74	4.91	3.83	5.96
Total Copper	30	1.68	2.87	1.56	2.93	1.54	3.13	1.70	3.19	3.79	7.16
Dissolved Iron	30	148.1	192.7	192.5	268.4	151.2	185.7	138.5	204.3	151.7	204.9
Total Lead	30	1.09	2.95	1.14	3.77	2.05	4.59	2.07	4.53	2.69	4.54
Dissolved Aluminum	30	65	139	100	177	73	124	67	137	87	141
Oil and Grease	15	0.4	1.7	0.4	1.5	0.5	1.9	0.5	2.0	0.0	0.0
Diesel Range Organics	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gasoline Range Organics	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lube Oil Range Organics	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total Petroleum Hydrocarbons	15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

fewer divalent cations (hardness) and more total lead than the river upstream of the study. Lead levels across samples sites are below protective standards.

Principal components analysis (PCA) creates linear combinations of variables that can be used to reduce the dimensions of a complex, multivariate dataset into fewer and easier to visualize components. The first two components of a PCA performed on the measured water quality variables explained 57.6% of the variability in the underlying dataset (Figure 5). Variables listed on the PCA axes represent the most important or most heavily loaded (largest coefficient) variables for that axis. The first (horizontal) PCA axis explained 40.51% of total dataset variability. Color, chromium, lead, and aluminum had the largest positive loadings, while alkalinity, hardness, chloride, and conductivity had the most negative loadings.

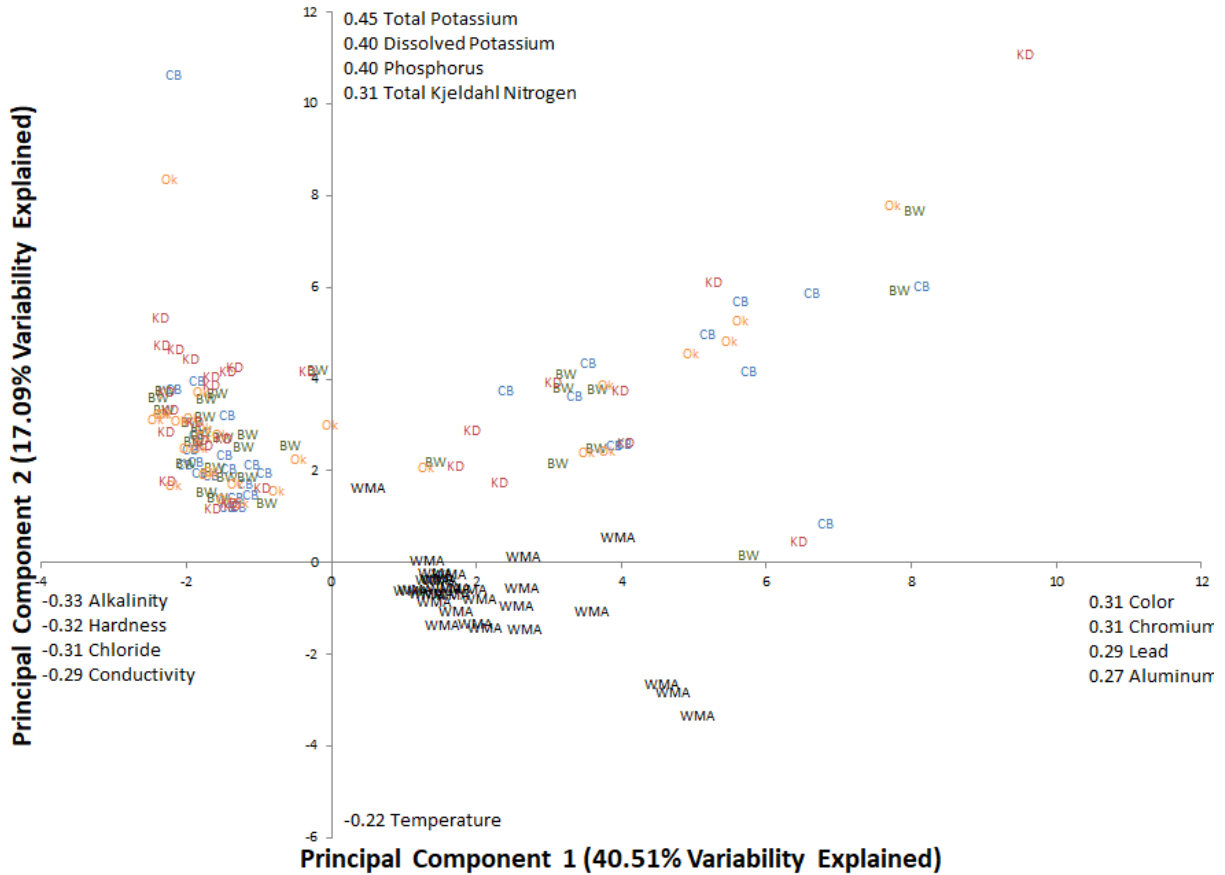


Figure 5. Principal components analysis of water quality variables. The four largest positive and negative loadings for each axis are at the relative terminus. Samples are plotted and markers are text and color indicating sample site as follows: WMA (Okmulgee Wildlife Management Area, black), Kelco discharge (KD, red), upstream of Okmulgee Creek (OK, orange), Budweiser tract (BW, green), and Coalton Bridge (CB, blue).

The variables with positive loadings were positively correlated with stream discharge (value increases with discharge). Conversely, the variables with negative loadings were negatively correlated with stream discharge (value decreases with discharge). Taken together, the positive and negative loadings on the first (horizontal) axis act as a surrogate for discharge, with base flow conditions on the left and flood conditions on the right. The second (vertical) PCA axis explained 17.09% of dataset variability and represented the major components of the CP Kelco (Kelco) discharge (potassium, phosphorus, and nitrogen). Most of the WMA (reference) samples were associated with negative values on the second axis, while samples collected below the Kelco discharge all occur on the positive end of the vertical axis. Based on the PCA, stream discharge is the most important factor controlling measured water quality variables, followed by the Kelco discharge.

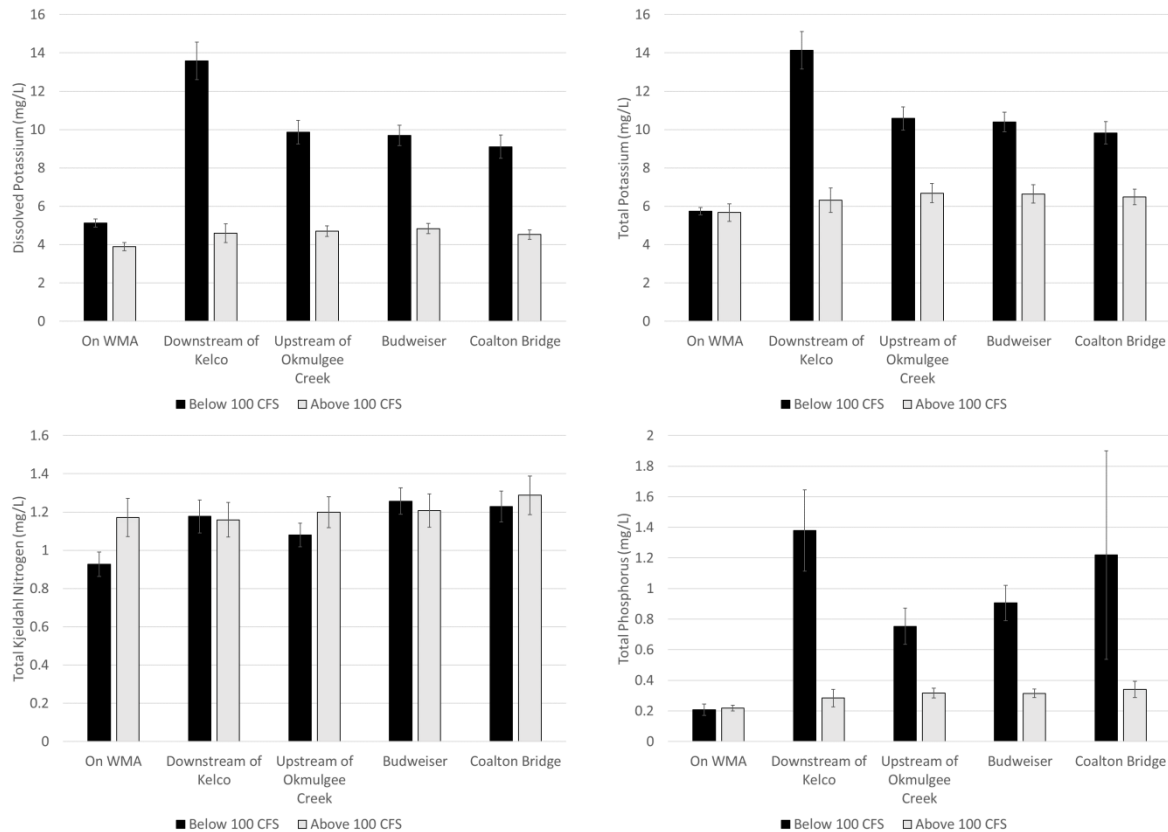


Figure 6. Dissolved potassium (top left), total potassium (top right), TKN (bottom left), and total phosphorus (bottom right) concentrations by sample site for low (less than 100 cubic feet per second, black bars, N=19) and high (greater than 100 cubic feet per second, grey bars, N=11) flows. Sites are ordered upstream to downstream from left to right. Error bars are standard error of the mean for each subset.

Four measured water quality parameters (dissolved and total potassium, total phosphorus, and total Kjeldahl nitrogen) varied depending on both stream discharge and site (Figure 6, Kelco discharge and downstream sites). Freshwater mussels are more sensitive to potassium concentrations, compared to other aquatic organisms. Wang et al. (2017) demonstrated that total potassium concentrations of 46 mg/L caused acute toxicity over a 48 hour period to 50% of tested fatmucket (*Lampsilis siliquoidea*) mussels. No samples came within 50% (maximum measurement of 21.5 mg/L or 47%) of the reported total potassium EC50. According to Wikipedia (2019), the half maximum effective concentration, EC50, refers to the concentration of the parameter which induces a response halfway between the baseline and maximum after a specified exposure period. However, recent research shows that potassium concentrations in the Kelco discharge reaches 195 mg/L K, or 4.2 times the reported 48 hour EC50 (Kunz et al. 2017). The same study also demonstrated that fatmuckets were more sensitive to potassium with increasing time, resulting in measured lowest observed effects concentrations (LOEC) of about 25 mg/L K. Taken together these results indicate that the high potassium effluent discharged during low flows at the Kelco site is toxic to freshwater mussels and measured potassium concentrations in the river were similar to the 7 day LOEC for fatmucket mussels.

References

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APPENDIX A. AREAS WITH WATERS OF RECREATIONAL AND/OR ECOLOGICAL SIGNIFICANCE

The following is a list of national and state parks, national forests, wildlife areas, wildlife management areas, and wildlife refuges within the study area which contain waters of recreational and/or ecological significance.

Deep Fork National Wildlife Refuge – WQM Segment No. 520700

Okmulgee Wildlife Management Area – WQM Segment No. 520700

Appendix B. QUALITY ASSURANCE AND QUALITY CONTROL

Replicate sample locations were chosen randomly before the start of field work. The majority of analytes were found to have mean absolute differences (the mean of the absolute value of the difference between paired sample and replicate) between the sample and replicate of less than 10% (Table B.1). True color (15%), total chromium (19%), nitrate + nitrite as N (45%), and oil and grease (41%) all had mean absolute percent differences greater than 10%. Only true color also had a correspondingly high standard deviation. The other analytes with large differences had large differences because measurements were close to minimum detection limits resulting in inflated relative differences.

Table B.1. Analysis of replicate samples. Replicate samples separated in the field and analyzed at the ODEQ lab are presented below as mean absolute percent difference between regular sample and the replicate sample. Maximum and minimum are presented as mean difference between regular sample and the replicate sample.

Analyte	N	Difference	Standard Deviation	Maximum	Minimum
True Color	30	14.90%	28.22%	118.18%	-8.33%
Total Dissolved Solids (mg/L)	15	1.33%	6.57%	8.70%	-17.95%
Total Alkalinity (mg/L)	30	0.51%	1.52%	5.98%	-1.67%
Total Hardness (mg/L)	30	2.75%	3.49%	15.50%	-8.96%
Chloride (mg/L)	30	1.80%	0.84%	1.48%	-2.00%
Sulfate (mg/L)	30	1.35%	4.59%	8.62%	-19.73%
Cyanide (mg/L)	30	1.84%	0.00%	0.00%	0.00%
Aluminum - Dissolved (µg/L)	30	8.22%	43.83%	125.32%	-100.00%
Chromium - Total (µg/L)	30	18.67%	7.62%	32.84%	-11.11%
Copper - Total (µg/L)	30	4.88%	8.54%	36.97%	-13.64%
Iron - Dissolved (µg/L)	30	2.41%	49.90%	98.35%	-100.00%
Lead - Total (µg/L)	30	N/A	2.20%	1.64%	-6.90%
Potassium - dissolved (mg/L)	30	7.69%	8.28%	23.19%	-19.44%
Potassium - Total (mg/L)	30	6.09%	2.63%	5.41%	-6.27%
Ammonia (mg/L)	30	0.76%	1.52%	8.33%	0.00%
Total Kjeldahl Nitrogen (mg/L)	30	3.40%	9.83%	36.15%	-5.81%
Nitrate+Nitrite as N (mg/L)	30	44.97%	1.27%	3.33%	-3.45%
Total Phosphorus (mg/L)	30	4.10%	5.67%	9.50%	-23.33%
Oil and Grease (mg/L)	15	41.32%	1.31%	5.06%	0.00%
Diesel Range Organics (mg/L)	15	0.00%	0.00%	0.00%	0.00%
Gasoline Range Organics (mg/L)	15	0.00%	0.00%	0.00%	0.00%
Lube Oil Range Organics (mg/L)	15	0.00%	0.00%	0.00%	0.00%
Total Petroleum Hydrocarbons (mg/L)	15	0.00%	0.00%	0.00%	0.00%