

Water Quality Conditions During 2009
in the Vicinity of the Klamath Hydroelectric Project

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SUMMARY

Water quality monitoring in the vicinity of the Klamath Hydroelectric Project in 2009 was a continuation of monitoring that has occurred since 2000. In 2009 the program was developed in accordance with Interim Measure 12 of the 2009 Agreement in Principle (AIP) Monitoring Plan that was developed by PacifiCorp and state, federal, and tribal entities. Physical measurements were made and samples for analysis of water chemistry were collected at nine river and reservoir sites from above J. C. Boyle reservoir to below Iron Gate dam. Samples were collected at multiple depths in Iron Gate, Copco, and J. C. Boyle reservoirs, and from a single off-shore location at river sites. Samples for the 2009 baseline water quality monitoring program were collected monthly in May through December. Additional samples were collected biweekly below Iron Gate dam in May through October.

Constituents measured in 2009 were similar to those in prior years. Physical measurements included water temperature, pH, dissolved oxygen and specific conductance. Chemical measurements included forms of phosphorus and nitrogen. Newly added constituents in 2009 included carbonaceous biochemical oxygen demand (CBOD₅), particulate carbon, and particulate nitrogen.

The results of sample analysis for the baseline monitoring program were essentially similar to results from other years. A comparison of data from two river sites, above J. C. Boyle reservoir and below Iron Gate dam for all years of data revealed that overall average phosphorus and nitrogen concentrations were substantially lower below Iron Gate dam compared to above J. C. Boyle reservoir, and that annual average concentrations were consistently lower below Iron Gate dam than above J. C. Boyle. Suspended solids are also significantly lower below Iron Gate dam. A similar comparison of data from the surface regions of Copco and Iron Gate reservoirs showed little difference in average nutrient concentration, chlorophyll *a*, or suspended solids between the reservoirs. Values for those constituents were more variable, sometimes substantially so, in Copco reservoir compared to Iron Gate reservoir.

INTRODUCTION

This report presents the results of the monitoring of water quality conditions during 2009 in the vicinity of the Klamath Hydroelectric Project (Project), located along the upper Klamath River in Klamath County, south-central Oregon, and Siskiyou County, northern California.

The water quality monitoring in 2009 was a continuation of similar monitoring conducted by PacifiCorp Energy (PacifiCorp) in 2000, 2001, 2002, 2003, 2004, 2005, 2007¹ and 2008 to characterize water quality conditions in the Project area. Results of water quality monitoring in these previous years are described in other documents (PacifiCorp 2004a, 2004b, 2006, 2007a, 2007b; Raymond 2008, 2009); these documents and the data are available on PacifiCorp's Project website at <http://www.pacificorp.com/es/hydro/hl/kr.html>. Water quality monitoring in 2009 was done in accordance with the 2009 Agreement in Principle (AIP) Monitoring Plan that was developed by PacifiCorp and state, federal, and tribal entities. Interim Measure 12 of the AIP stipulates to a water quality monitoring program, including on-going monitoring of blue-

¹ Water quality sampling was not conducted in 2006.

green algae (cyanobacteria) and associated toxins. The 2009 AIP Plan included two components, public health monitoring of cyanobacteria and toxins, and comprehensive baseline water quality monitoring of the Klamath River. This report summarizes the results of the portion of the baseline water quality monitoring conducted by E&S Environmental Chemistry, Inc. for PacifiCorp. The 2009 AIP Plan is available on the California Northcoast Regional Board's website (www.waterboards.ca.gov/northcoast/water_issues/programs/tmdls/klamath_river/).

The objectives of the 2009 baseline water quality monitoring program included the following:

- Improve the current understanding of seasonal, annual, and long-term variations in a wide range of water quality parameters for Klamath River from Link dam to the estuary.
- Form a long-term program that captures the effects of activities in the system potentially affecting water quality in the Klamath River.
- Provide a long-term baseline data set of water quality conditions that can be readily extended to assess impacts of management actions and restoration processes.
- Collect data under a consistent Quality Assurance (QA) framework
- Disseminate data in a timely fashion.

The 2009 baseline water quality monitoring included five components, including:

- measurements of physical water quality parameters (water temperature, dissolved oxygen, pH, and specific conductance) with multi-probe instrumentation
- grab samples for laboratory analysis of water chemistry (forms of nitrogen and phosphorus, suspended solids, and dissolved organic carbon)
- deployment of a data sonde to continuously record physical water quality parameters in the Klamath River below Iron Gate dam
- deployment of thermographs to continuously record water temperature at seven sites upstream, within, and downstream of the Project area
- sampling for phytoplankton abundance and microcystin

This report presents the results of the water chemistry and physical measurements. The results of the data sonde and thermograph deployments will be reported separately.

Sites

Physical measurements were made and samples for analysis of water chemistry were collected at nine river and reservoir sites from above J. C. Boyle reservoir to below Iron Gate dam. Table 1 identifies the site locations associated with the five components of the water quality monitoring program. River miles for the site locations refer to distance from the mouth of the Klamath River. Sample site locations on the Klamath River are shown in Figure 1. Samples were collected once, in January, from the mouth of Link River (River Mile [RM] 253), below Keno dam (RM 233), Collier rest area at I-5 (RM 179), and Walker Bridge (RM 157) under the 2008 work plan.

Samples were collected at multiple depths in Iron Gate, Copco, and J. C. Boyle reservoirs, and from a single off-shore location at river sites. Temperature data loggers were installed at seven locations in the Klamath River between Keno dam and the I-5 freeway. A continuous-recording multiprobe data sonde was installed in the Klamath River just below Iron Gate dam in 2008 and is operated year round.

Table 1. Sample sites and associated water quality sub-programs.

Location	Site ID	River Mile	Chemistry Sampling	Physical Measurements	Data sonde	Thermograph	Phytoplankton Sampling
Klamath R. above J.C. Boyle reservoir	KR22822	228.2	X	X		X	X
J.C. Boyle reservoir near dam	KR22478	224.8	X	X			X
Below J.C. Boyle dam	KR22460	224.6	X	X			X
Klamath R. below J.C. Boyle powerhouse	KR22000	220.0	X	X		X	X
Klamath R. above Shovel Creek	KR20642	206.4	X	X		X	X
Copco reservoir lower end at log boom	KR19874	198.7	X	X		X	X
Klamath R below Copco 2 powerhouse	KR19645	196.3	X	X			X
Iron Gate reservoir lower end above log boom	KR19019	190.2	X	X		X	X
Klamath R. at Iron Gate Hatchery bridge	KR18973	189.7	X	X	X		X

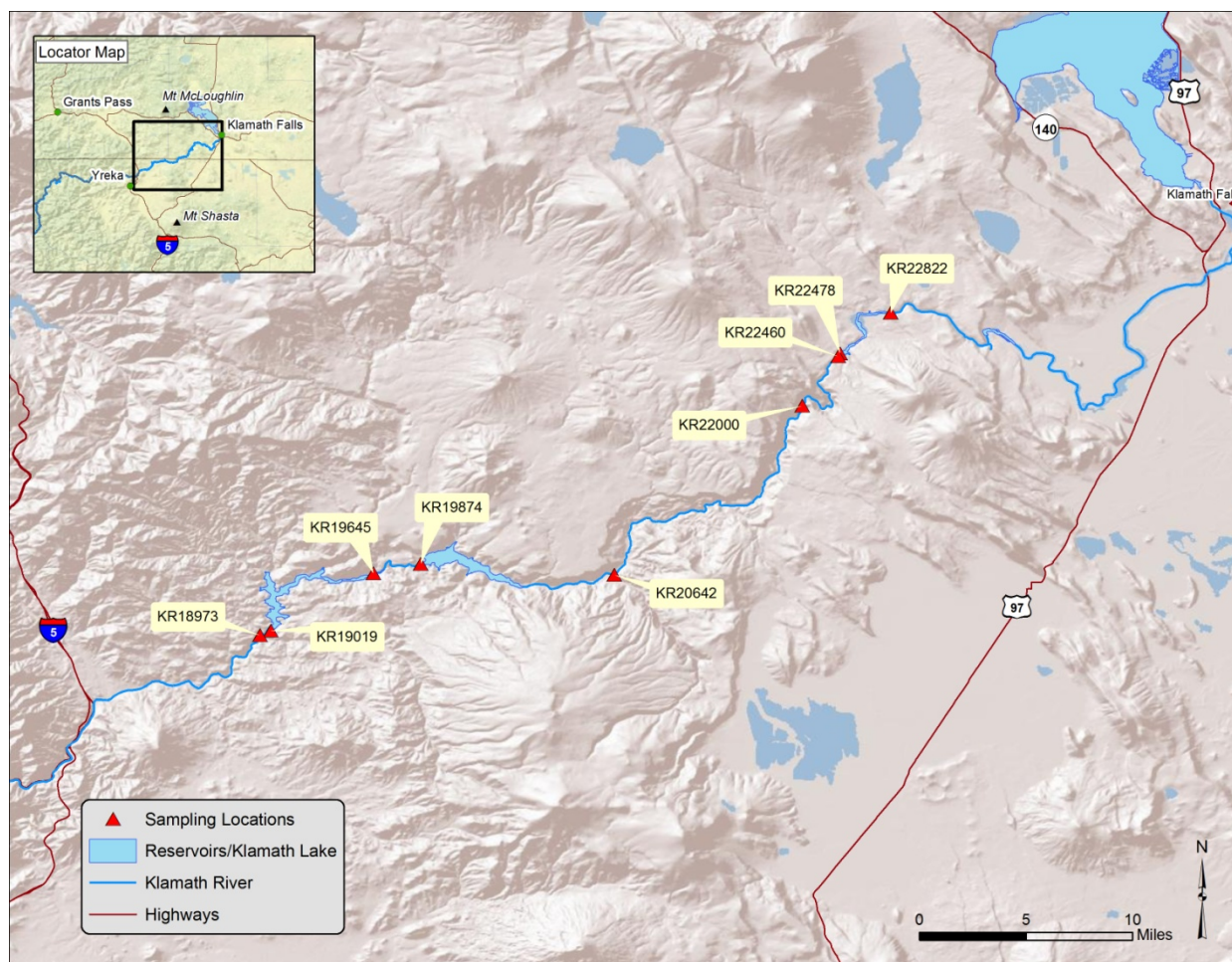


Figure 1. The locations of PacifiCorp water quality sampling sites during 2009 in the vicinity of the Klamath River Hydroelectric Project.

Results for chemistry sampling and physical measurements are described in this report. Data sonde data are available at the PacifiCorp website. Thermograph data will also be made available on the PacifiCorp website.

Schedule

Samples for the 2009 baseline water quality monitoring program were collected monthly in May through December. Additional samples were collected biweekly below Iron Gate dam in May through October. The monthly sampling events in 2009 occurred during the weeks of January 14, May 23, June 22, July 20, August 17, September 14, October 12, November 17, and December 13.

METHODS

Field Methods

Sampling included instantaneous field measurements of physical parameters (with multi-probe instrumentation) and collection of grab samples for laboratory analysis of water chemistry. Physical measurements for water temperature, pH, conductivity, dissolved oxygen, and oxidation-reduction potential were made using an In-Situ MiniTroll 9000 multiparameter data sonde calibrated according to the manufacturer's instructions prior to each sampling event. Calibration was verified at the close of each sampling event.

In the reservoirs, *in situ* depth profile measurements were made to the bottom, at 1 m intervals in J. C. Boyle reservoir, 2 m intervals in Copco reservoir, and 3 m intervals in Iron Gate reservoir. The measurements were taken by lowering a multi-probe sensor unit to the depth intervals indicated above. Measurements at river sites were made by placing the sensor in the flow either by suspending it from a bridge or other structure or by placing it some distance away from the bank.

Water samples were collected using a Kemmerer water sampler. Grab samples from the river sites were collected by lowering the sampler into the current from a bridge, or by tossing the sampler into the current from the shore. The sampler was closed, retrieved, and emptied into a churn splitter that had been well-rinsed with sample water. Repeated casts with the sampler were made to obtain sufficient sample to fill all required sample containers. For reservoir samples the sampler was lowered to the desired depth and retrieved. Samples were dispensed directly from the sampler to containers supplied by the laboratory.

Grab samples from the reservoir sites were collected at discrete depths in the reservoirs using a Kemmerer sampler. Four samples were taken from the deepest site in Copco reservoir near the log boom, including at 0.5, 9, 18, and 27 meters below the surface. Five samples were taken from the deepest site in Iron Gate reservoir near the log boom, including at 0.5, 10, 20, 30, and 40 meters below the surface. Two samples were taken from J. C. Boyle reservoir at 0.5 m and 8.0 m below the surface.

In the reservoirs, two phytoplankton samples were collected at each site. In Copco and Iron Gate reservoirs one grab sample was collected at 0.5 m depth. A second sample, integrated over a depth of 8 m was collected by lowering a tube to 8 m, closing and retrieving the tube, emptying

the tube into a container, mixing, and dispensing the sample into sample containers. In J. C. Boyle reservoir two samples were collected, one each at 0.5 m and 8.0 m depth.

All samples were kept on ice, in the dark, in coolers, and shipped or hand delivered to the laboratories to meet specified holding times.

Samples were analyzed for ammonia (NH₃), nitrate + nitrite (NO₃), total nitrogen (NT) as N, total phosphorous (PT), orthophosphate (PO₄), dissolved organic carbon (DOC), total alkalinity, carbonaceous oxygen demand (CBOD), chlorophyll *a*, particulate carbon, particulate nitrogen, total suspended solids (TSS), and volatile suspended solids (VSS) using methods as summarized in Table 2. Samples were also analyzed for algae speciation, abundance, and biovolume.

Lab Methods

Water samples were analyzed for a variety of constituents by the CH2M Hill Applied Sciences Laboratory, Chesapeake Biological Laboratory, and EPA Region 9. Phytoplankton samples were analyzed for abundance and species composition by Aquatic Analysts of Friday Harbor, Washington. Some constituents with short hold times (PO₄) were analyzed in the field by E&S Environmental Chemistry using a Hach Model DR2400 field spectrophotometer. The constituents measured and methods used are shown in Table 2.

Table 2. Analytical methods for 2009 water quality sampling.

Constituent Name	Constituent Code	Analysis Method	MDL	MRL	Units
Dissolved organic carbon	DOC	EPA415.1	0.036	0.5	mg/L
Carbonaceous oxygen demand	CBOD	SM5210B	NA	2.0	mg/L
Particulate carbon	PC	EPA 440	0.02	0.05	mg/L
Particulate nitrogen	PN	EPA 440	0.02	0.05	mg/L
Total nitrogen	NT	SM4500-N B	0.018	0.20	mg/L
Ammonia nitrogen (as N)	NH ₃	EPA350.1	0.0078	0.10	mg/L
Nitrate+nitrite nitrogen (as N)	NO ₃	EPA353.2	0.0057	0.01	mg/L
Total phosphorus (as P)	PT	EPA365.1	0.0078	0.05	mg/L
Orthophosphate (as P)	PO ₄	Field spectrophotometer (EPA365.1)	NA	0.05	mg/L
Total suspended solids	TSS	EPA160.2	1.23	2.0	mg/L
Volatile suspended solids	VSS	EPA160.4	2.46	2.0	mg/L
Chlorophyll <i>a</i>	CHLA	SM10200H.3	0.00001	0.02	µg/L
Alkalinity	ALKT	EPA310.1	2.17	5	mg/L
Phytoplankton abundance	PPLK	SM10200F	1	1	count
Microcystin	MYCN	ELISA	NA	0.16	mg/L
Water temperature	TEMP	In-situ probe	NA	NA	°C
Dissolved oxygen	DOCON	In-situ probe	NA	1.0	mg/L
Specific conductance	SPC	In-situ probe	NA	5	µS/cm
pH	PH	In-situ probe	NA	0.1	units

Statistical Methods

Water quality data gathered in 2009 were examined using a variety of graphical and numerical methods. Graphics methods included box plots, scatter plots, and bar graphs. Numerical methods included calculation of summary statistics, comparison of confidence intervals, linear and non-linear regression. Graphical and numerical methods were carried out using a variety of statistical software including Minitab®, Statistix9®, XLStat®, and SigmaPlot®.

Quality Assurance

The Klamath relicensing water quality activities follow a defined quality control program (PacifiCorp 2008d) that includes internal quality control by the laboratories, external quality control by field crews, and functional quality control by administrative oversight.

The laboratory internal quality control follows the guidelines of the National Environmental Laboratory Accreditation Conference (EPA 2003), and includes the scrutiny of samples when delivered, and analysis of internal blanks and reference standards. When discrepancies are noted, or internal checks are not met, exception reports are generated and samples are reanalyzed.

The external quality assurance (QA) program operates through the use of field blanks, replicate samples, spikes, and reference standards. Field blanks, replicates, spikes, and reference standards are submitted to the lab at least once for every sample batch, and comprise approximately 10 percent of all samples analyzed. If data quality objectives are not met for the QA samples, they are reanalyzed if possible. All external QA check samples submitted to the laboratories are blind samples (sample is not identified as an external check sample). If the original analysis is not confirmed the entire batch may be reanalyzed.

The functional quality control (QC) program operates through careful training of field workers, careful scrutiny of data and field practice, and active laboratory oversight. When data are received they are examined for any anomalous values. If a suspected outlier is identified, the field notes are examined to verify that all is in order, the field staff are interviewed to identify any conditions that may have affected the sample, the laboratory results sheets are examined, and the laboratory program manager contacted to verify the result. If no explanation for the anomalous value can be found, it is retained in the data set.

Data quality objectives are established for the external QA check samples submitted to the laboratories with the regular samples. These objectives establish whether data generated from the laboratory analyses are reliable. For this program, data quality objectives are established for accuracy, precision, and completeness.

Accuracy is the degree of agreement of a measurement with an accepted reference or true value. It is most frequently expressed as percent recovery. Precision is a measure of the mutual agreement (or variability) among individual measurements of the same property, and is usually expressed as relative percent difference (RPD). Completeness is the measure of the number of valid measurements obtained from a measurement system compared to the total number of measurements that was expected to be obtained under correct normal sampling conditions. It is usually expressed as a percentage. Details of the QA program are provided in the Appendix.

RESULTS

This section presents the results obtained during the 2009 baseline water quality monitoring program. The results are presented in separate sections for river sites and reservoir sites. There were a total of 230 samples collected for water quality analyses during 9 planned sampling events in 2009. Sampling occurred in January and May through December.

River Sites – *In Situ* Measurements

Water quality conditions at the river sites varied by season and through the Project area. Summary statistics for *in situ* measurements of physical constituents at the river sites are shown in Table 3.

Table 3. Summary statistics for *in situ* measurements at Klamath River sites in 2009.

	Dissolved Oxygen (mg/L)	Dissolved Oxygen (Percent Saturation)	Specific Conductance ($\mu\text{S}/\text{cm}$)	Temperature ($^{\circ}\text{C}$)	pH (units)
N	48 ^a	48	53	53	53
Mean	10.4	106.3	172	13.3	7.9
Std. Dev.	2.1	15.9	24	8.1	0.4
Minimum	7.9	77.8	140	0.8	7.3
Median	10.3	106.0	168	16.6	7.8
Maximum	17.6	156.5	233	25.2	8.8
MAD ^b	1.2	11.6	18	5.7	0.2

^a There are fewer results for D.O. because the instrument failed during one event (Aug. 19)

^b MAD = median absolute deviation

Temperature

Water temperatures in the Klamath River in the vicinity of the Project ranged from a minimum of 0.8 $^{\circ}\text{C}$ below J.C. Boyle dam (KR22460) in December to a maximum of 25.2 $^{\circ}\text{C}$ above J.C. Boyle dam (KR22822) in July. Mean temperature for all sites and dates was 13.3 $^{\circ}\text{C}$. There was no evident trend in temperature with river mile (Figure 2). Temperatures at river mile 228 did not show the low values seen at other sites because the location was inaccessible because of snow during the coldest months, and no data were gathered. Temperature showed a distinct seasonal pattern (Figure 2).

pH

Values for pH in 2009 ranged from a low of 7.3 at Spring Island below the J. C. Boyle powerhouse (KR22000) on June 23rd to a high of 8.8 near the hatchery bridge below Iron Gate dam (KR18973) on August 18th. The average pH for all sites and dates was 7.9. There did not appear to be a significant difference in pH among the sites sampled, however, pH was more variable below Iron Gate dam (RM 198) and above Copco reservoir (RM 206), and tended to be somewhat lower below J. C. Boyle reservoir than at other sites. There was evidence of a seasonal pattern with low values at most sites during the winter and higher values during the summer. Peaks in May and September were separated by lower values in June through August (Figure 3).

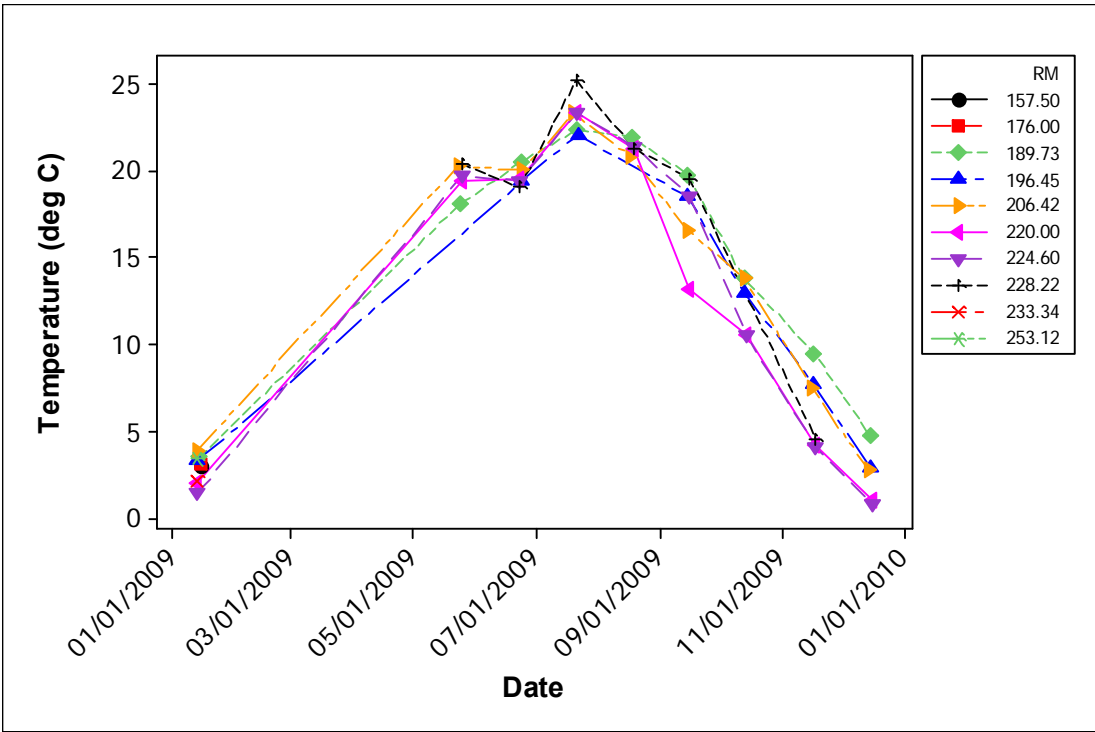
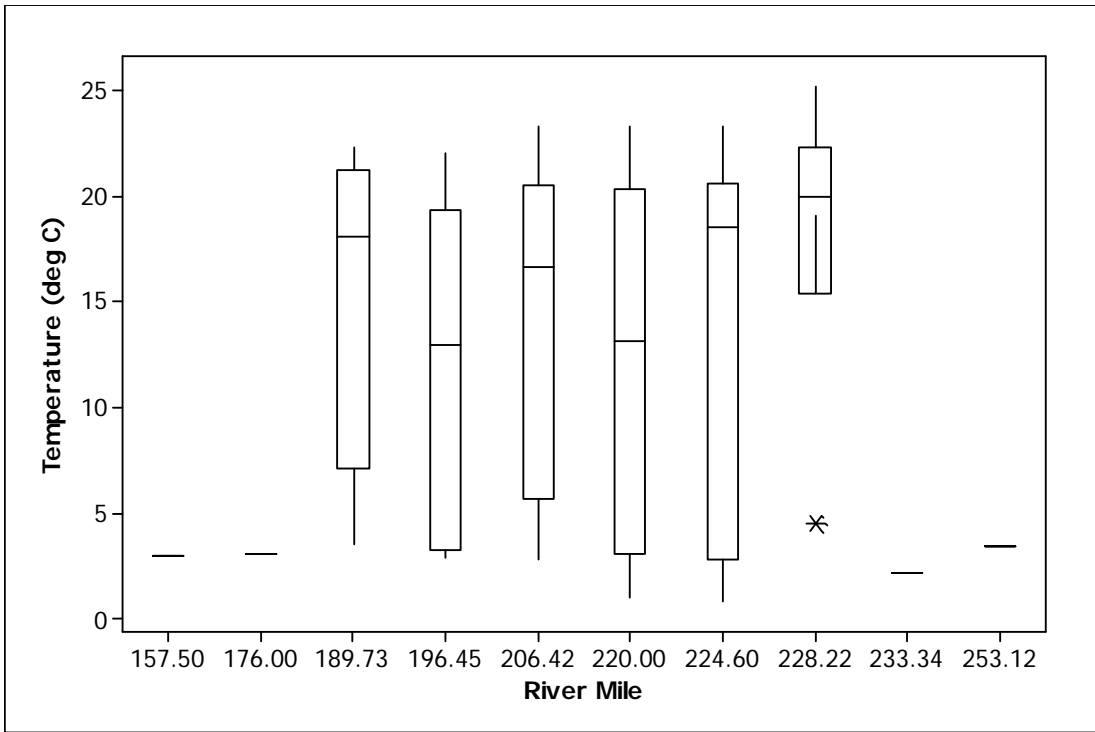


Figure 2. Water temperature values measured at various sites in the Klamath River in 2009, plotted against river mile.

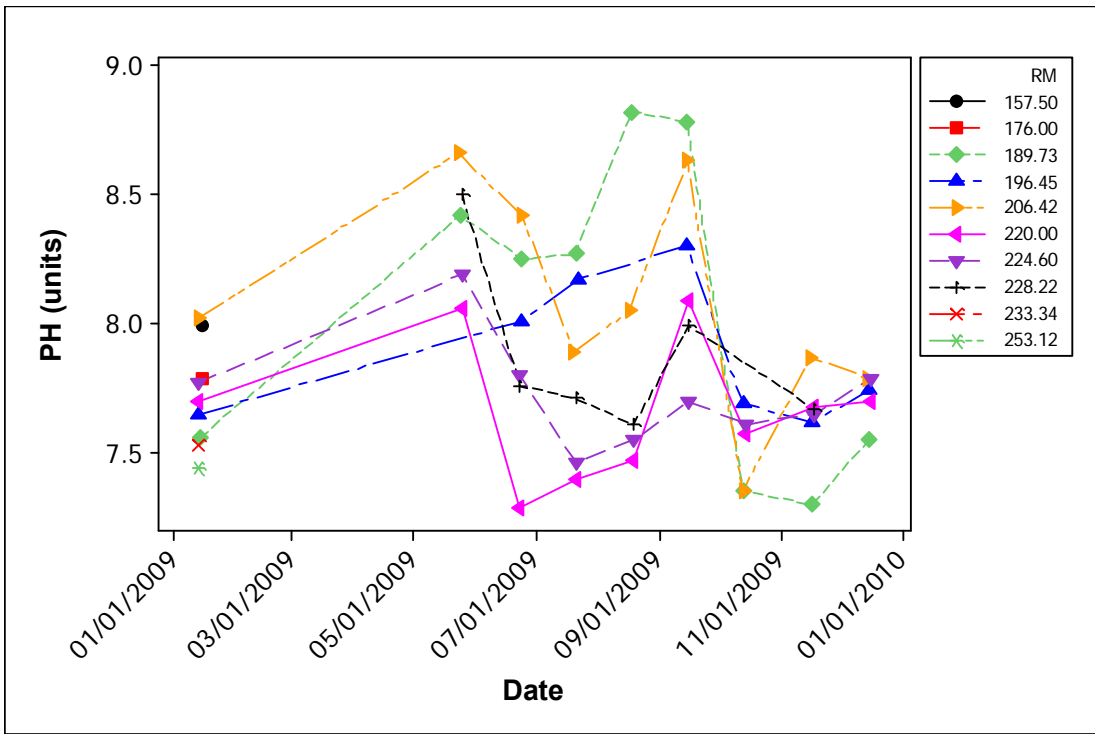
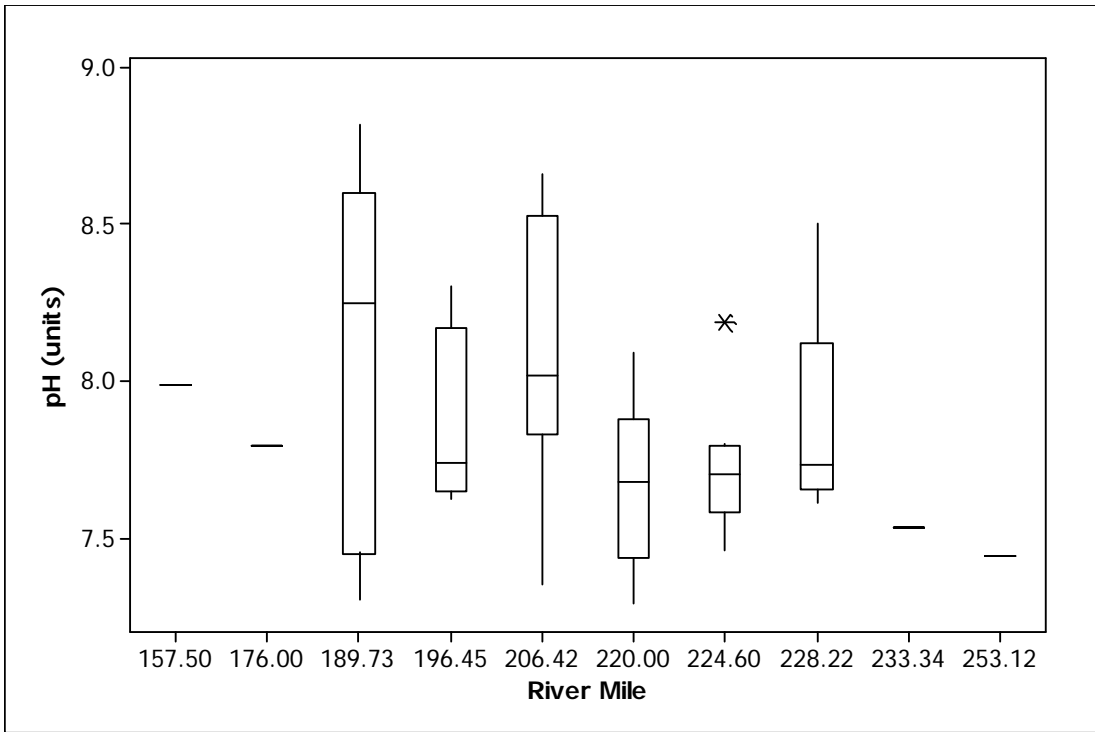


Figure 3. pH values measured at various sites in the Klamath River in 2009, plotted against river mile.

Dissolved Oxygen

The lowest dissolved oxygen concentration measured at a river station in 2009 was 8.0 mg/L on June 23 above J. C. Boyle reservoir (KR22822,). The highest value was also at this site-the dissolved oxygen concentration measured on November 18th was 18.0 mg/L. The average dissolved oxygen value for all sites and dates was 10.0 mg/L. The median value for dissolved oxygen at the site above J. C. Boyle reservoir (KR22822) was lower than the sites downstream, and values were more variable, but there did not appear to be a significant difference among the sites (Figure 4). Dissolved oxygen values tended to be lower during the mid summer and higher in the fall and winter. Dissolved oxygen values were especially high in December (Figure 4).

Dissolved oxygen saturation (percent) ranged from a low of 77.8 percent measured above Iron Gate reservoir (KR19645) on January 13th to a high of 156.5 percent measured above J. C. Boyle reservoir (KR22822) on November 18th. Average percent saturation for all sites and times was 106.3 percent. Dissolved oxygen saturation did not show any significant spatial or seasonal trend. Percent saturation tended to be lower in November than other month, and was particularly low in January (Figure 5).

Specific Conductance

Specific conductance² (SPC) values ranges from a minimum of 140 $\mu\text{S}/\text{cm}$ measured above J. C. Boyle reservoir on September 16th, to a maximum of 233 $\mu\text{S}/\text{cm}$ measured below Keno dam (KR23334) on January 13th. Average SPC for all sites and dates was 172 $\mu\text{S}/\text{cm}$. The variability of SPC appeared to diminish with distance downstream, but there was little difference in the median value (Figure 6). The difference in SPC values measured in January between Link River (RM 253) and Keno dam (RM233), and between Highway I-5 (RM179) and Walker Bridge Road (RM 157) suggests that there is a source of water with high dissolved solids content between those pairs of sites. Sites above Copco reservoir showed a definite seasonal pattern in SPC with high values in January through June, low values in July through September, and higher but fluctuating values in October through December (Figure 6). This suggests a response to rapidly changing quality of the water entering the project from upstream. The pattern was less pronounced at sites below Copco reservoir, a result of the moderating influence of the reservoirs.

River Sites – Physical Measurements

Water samples collected in 2009 were analyzed for several physical constituents including total alkalinity, carbonaceous biological oxygen demand (CBOD), dissolved organic carbon, total suspended solids, and volatile suspended solids. Summary statistics for those constituents, measured at the river locations, are provided in Table 4.

² Specific conductance is conductivity adjusted to 25°C to remove the effect of temperature variation between measurements.

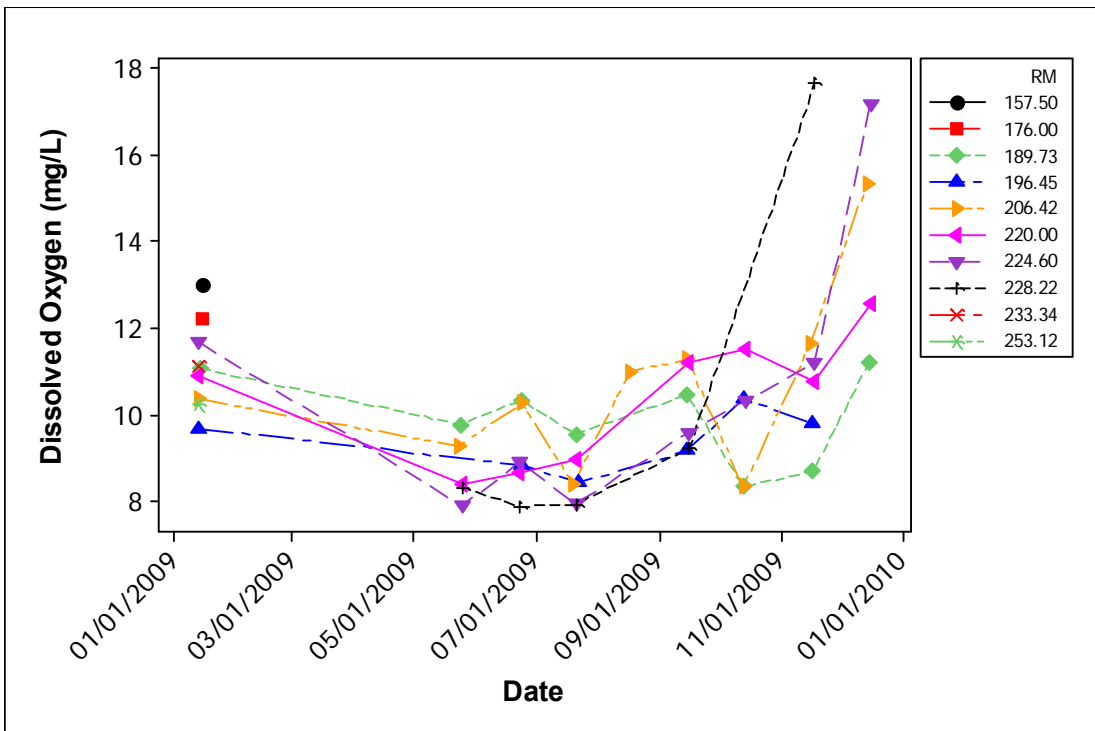
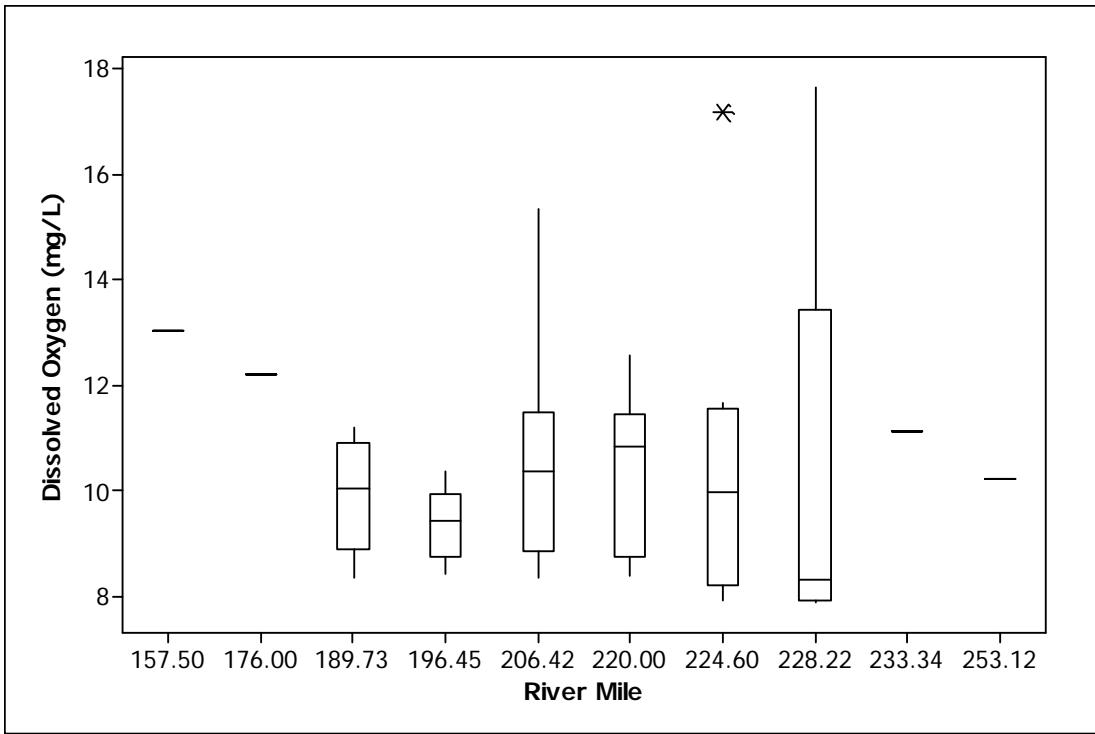


Figure 4. Dissolved oxygen concentration values measured at various sites in the Klamath River in 2009, plotted against river mile.

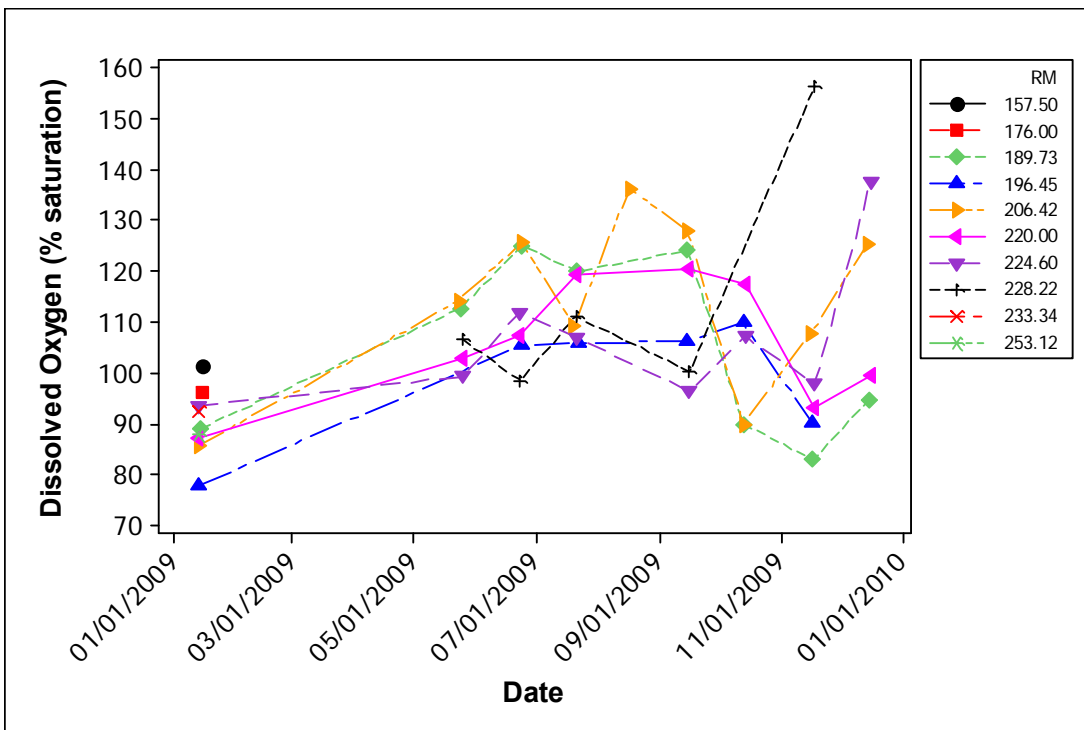
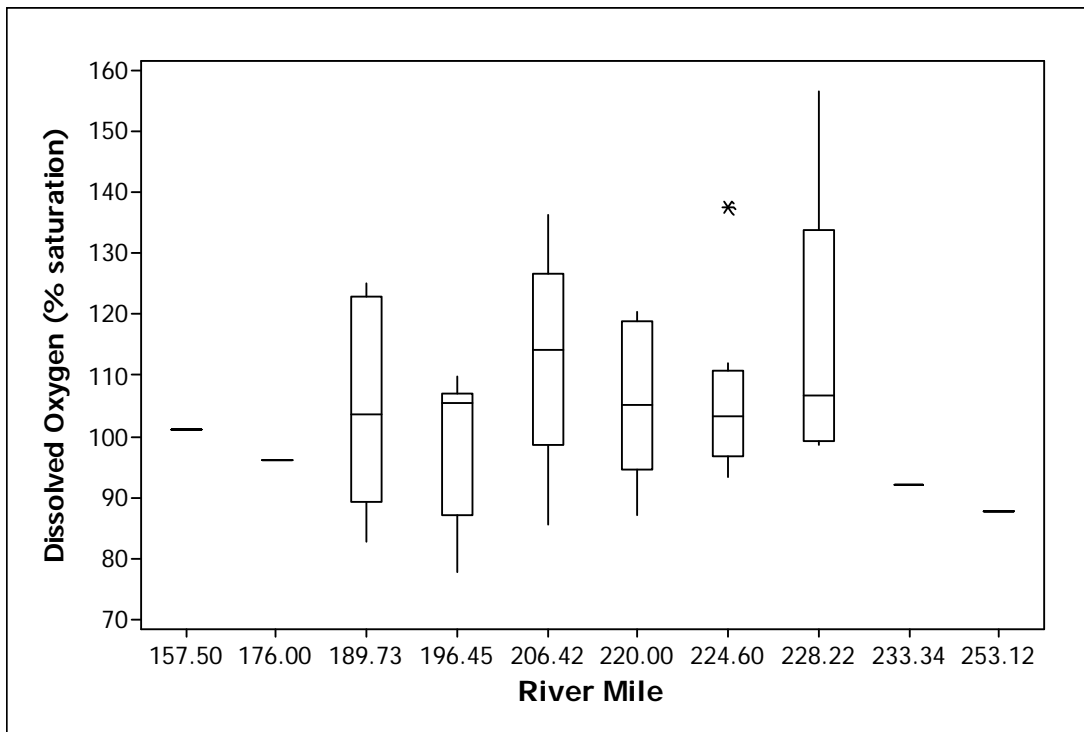


Figure 5. Dissolved oxygen saturation values measured at various sites in the Klamath River in 2009, plotted against river mile.

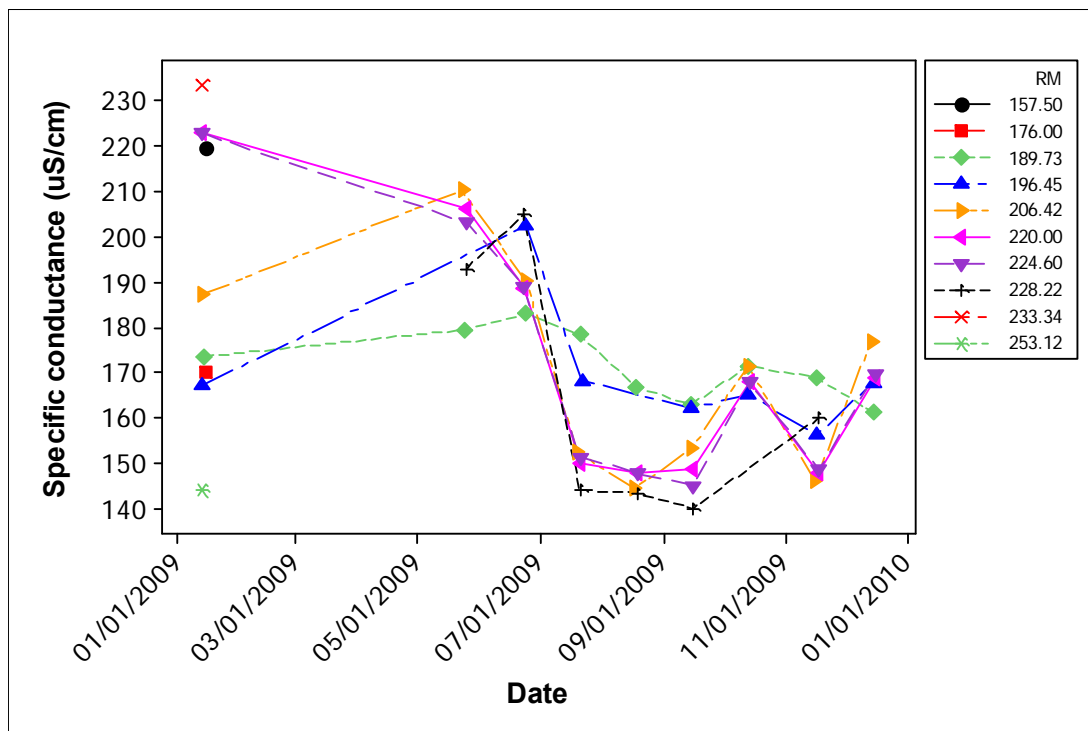
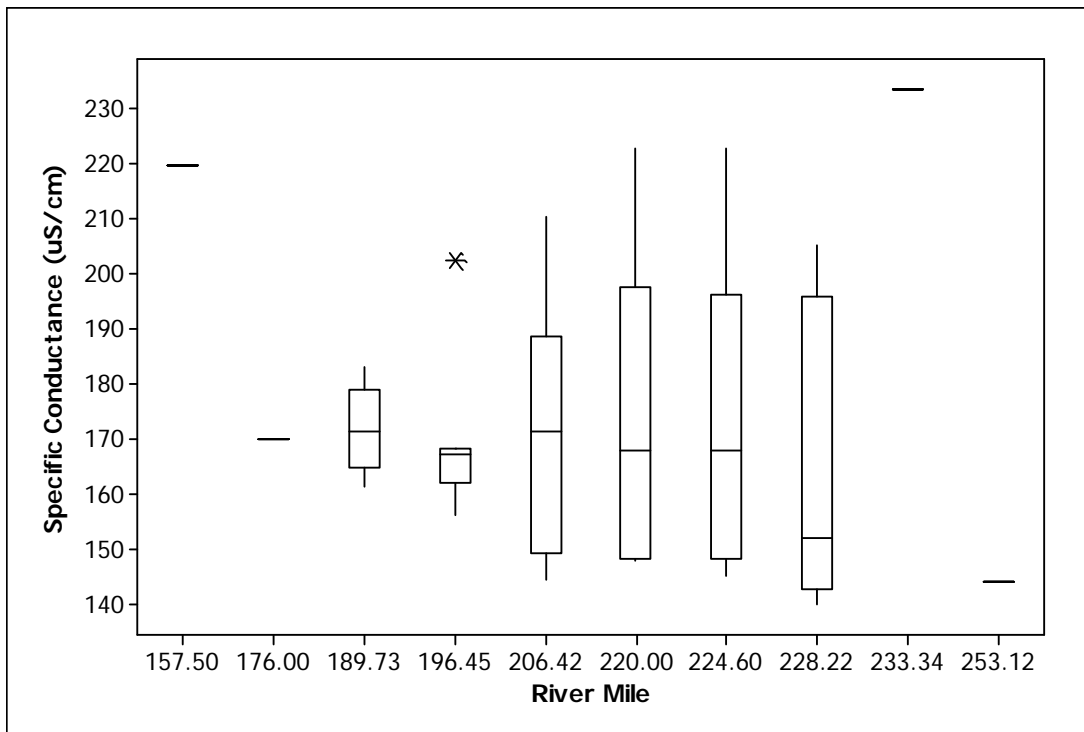


Figure 6. Specific conductance values measured at various sites in the Klamath River in 2009, plotted against river mile.

Table 4. Summary statistics for physical measurements at Klamath River sites in 2009.

	Alkalinity (mg/L as CaCO ₃)	CBOD ₅	Dissolved Organic Carbon (mg/L)	Total Suspended Solids (mg/L)	Volatile Suspended Solids (mg/L)
N	51 ^a	18 ^b	56	56	56
Mean	67.0	3.23	6.35	4.1	1.4
Std. Dev.	7.1	2.59	1.72	2.9	1.1
Minimum	54.0	0.00	2.56	0.4	0.0
Median	66.0	3.14	6.11	3.6	1.2
Maximum	83.6	7.62	9.78	13.2	4.0
MAD	5.4	2.10	1.18	1.2	0.8

^a Samples were not analyzed for alkalinity in May.

^b CBOD₅ was sampled at only two sites, KR20642 and KR18973.

Alkalinity

Alkalinity is an indirect measure of dissolved inorganic carbon in the water, assuming that the titratable base is entirely the result of carbonate compounds. The minimum value recorded for total alkalinity, in 2009 was 54 mg/L (as CaCO₃) above J. C. Boyle reservoir on September 19th, while the highest value was 83.6 mg/L measured below Keno dam on January 13th. The overall average value for alkalinity at the river sites was 67 mg/L. Alkalinity and SPC are both functions of dissolved ions, so the seasonal and spatial pattern of alkalinity and SPC were similar. However, the increase in the median alkalinity with distance downstream was more pronounced than that for SPC (Figure 7). The seasonal pattern for both constituents was similar.

Carbonaceous Oxygen Demand (CBOD)

CBOD was measured at only two sites, above Copco reservoir (KR20642) and below Iron Gate dam (KR18973). The median CBOD value below Iron Gate dam was slightly lower than above Copco reservoir, but the differences were not statistically significant (Figure 8). CBOD was highly variable from month to month but within that variability a slight increasing trend was discernable.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) together with particulate organic carbon provide an estimate of the organic carbon in the water. DOC values measured in the Klamath River in 2009 ranged from 2.56 mg/L at Spring Island below the J. C. Boyle powerhouse on September 16th to 9.78 mg/L below J. C. Boyle dam on June 23. The overall average value for dissolved organic carbon was 6.35 mg/L. Dissolved organic carbon tended to decrease with distance downstream between the site above J. C. Boyle reservoir (RM 228) and below Iron Gate dam (RM 189; Figure 9). DOC values tended to be higher in the summer than in the winter. The concentration of DOC at sites below Copco and Iron Gate dams was lower than at the other sites suggesting that DOC was retained or consumed in the reservoirs. Two especially low values of DOC at locations below J. C. Boyle powerhouse in September suggest that the samples were taken from the river when the flow was dominated by spring inflow.

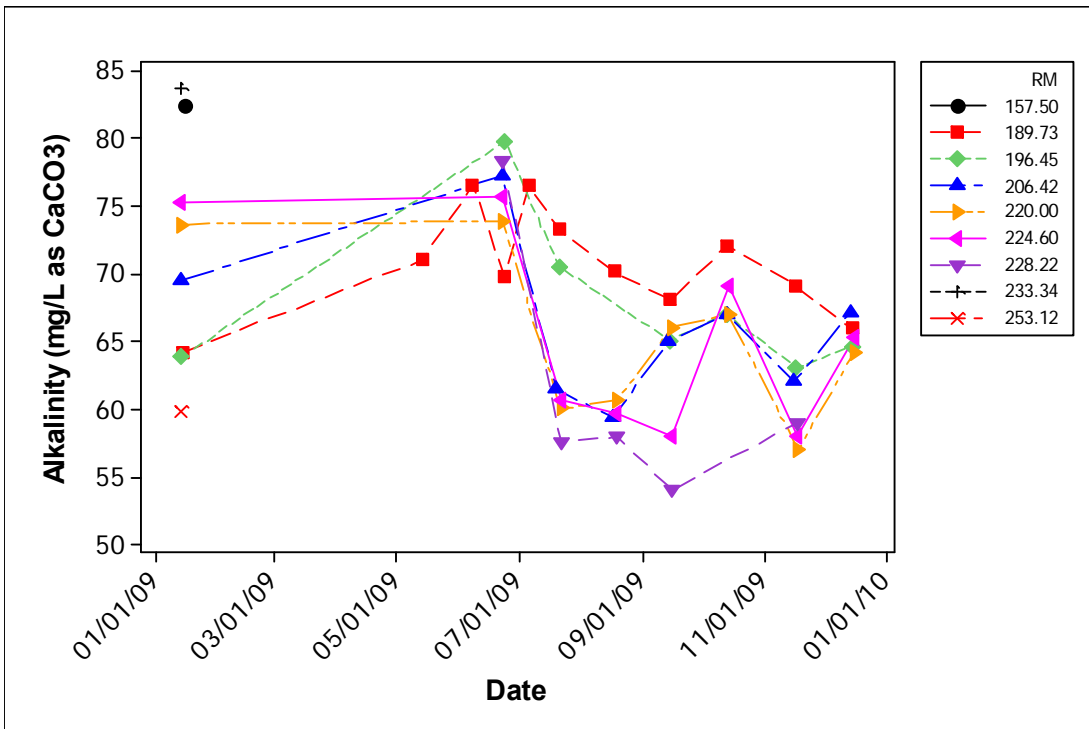
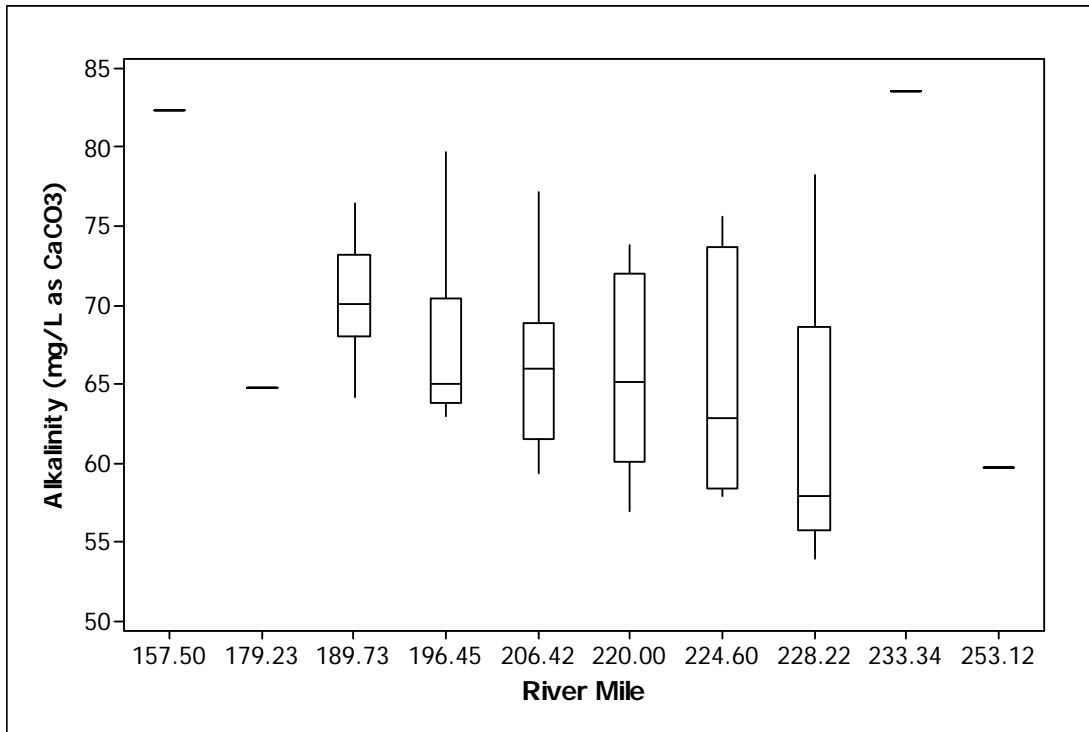


Figure 7. Alkalinity values measured at various sites in the Klamath River in 2009, plotted against river mile.

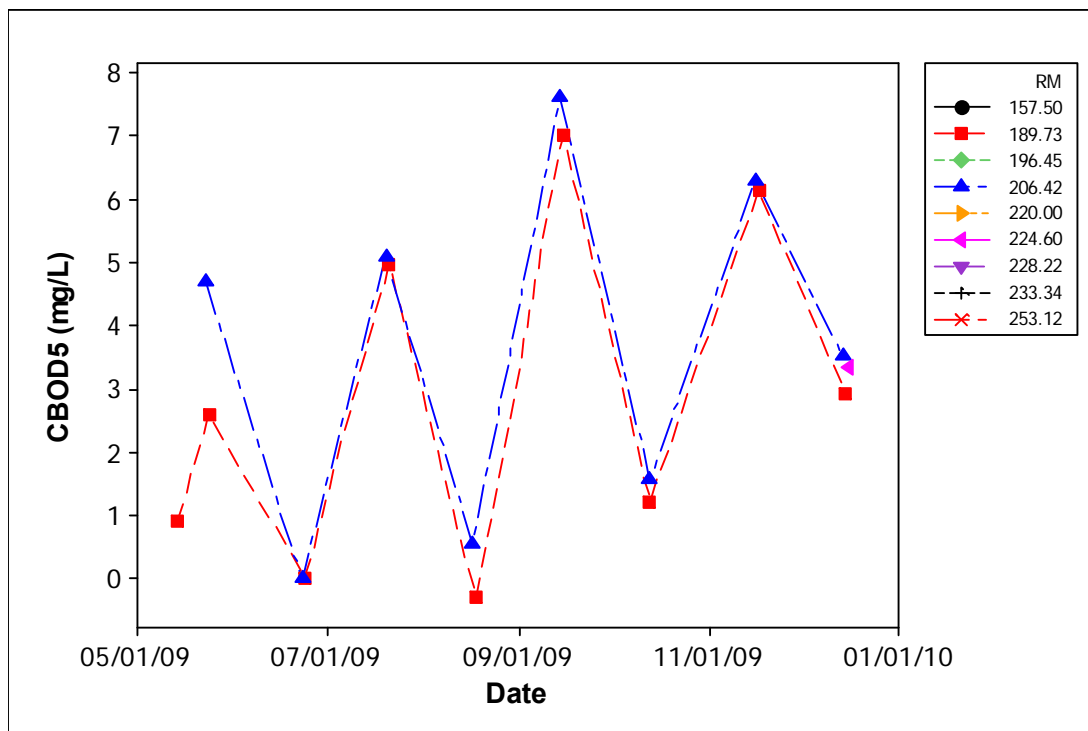
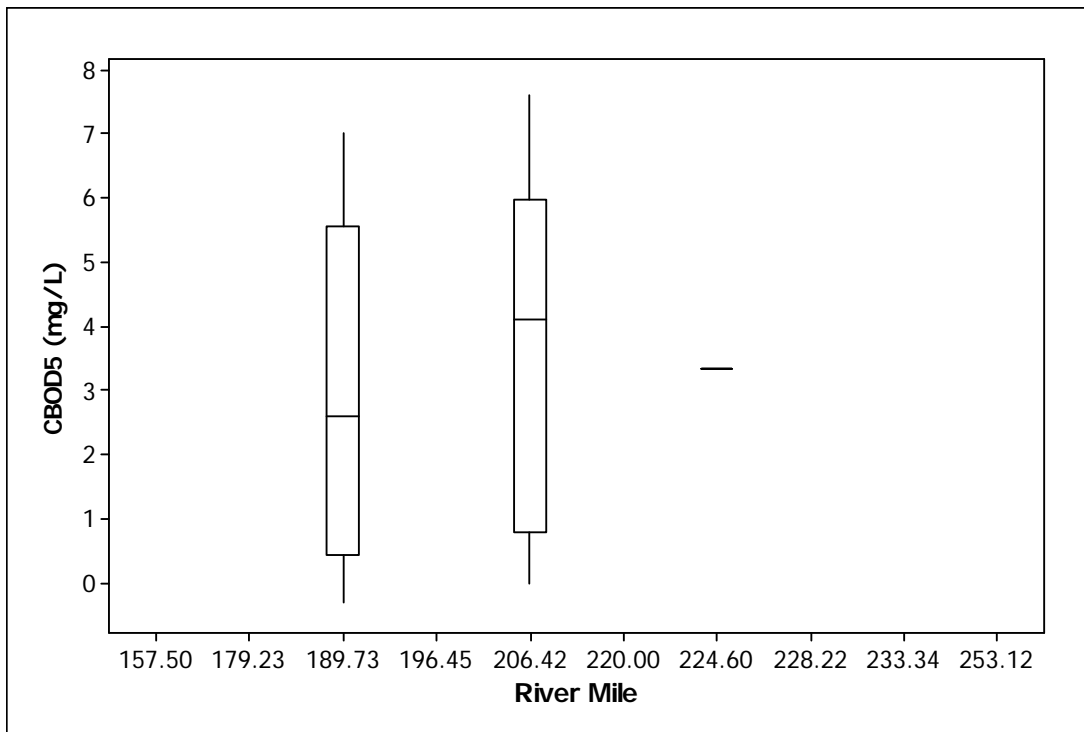


Figure 8. CBOD values measured at various sites in the Klamath River in 2009, plotted against river mile.

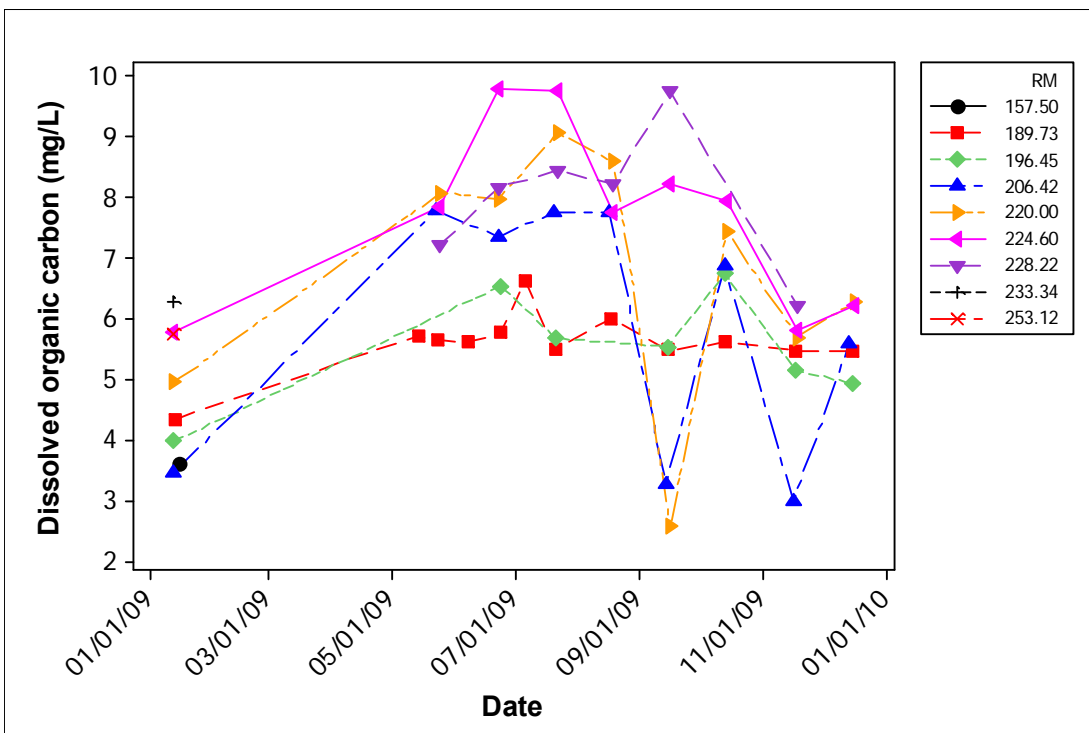
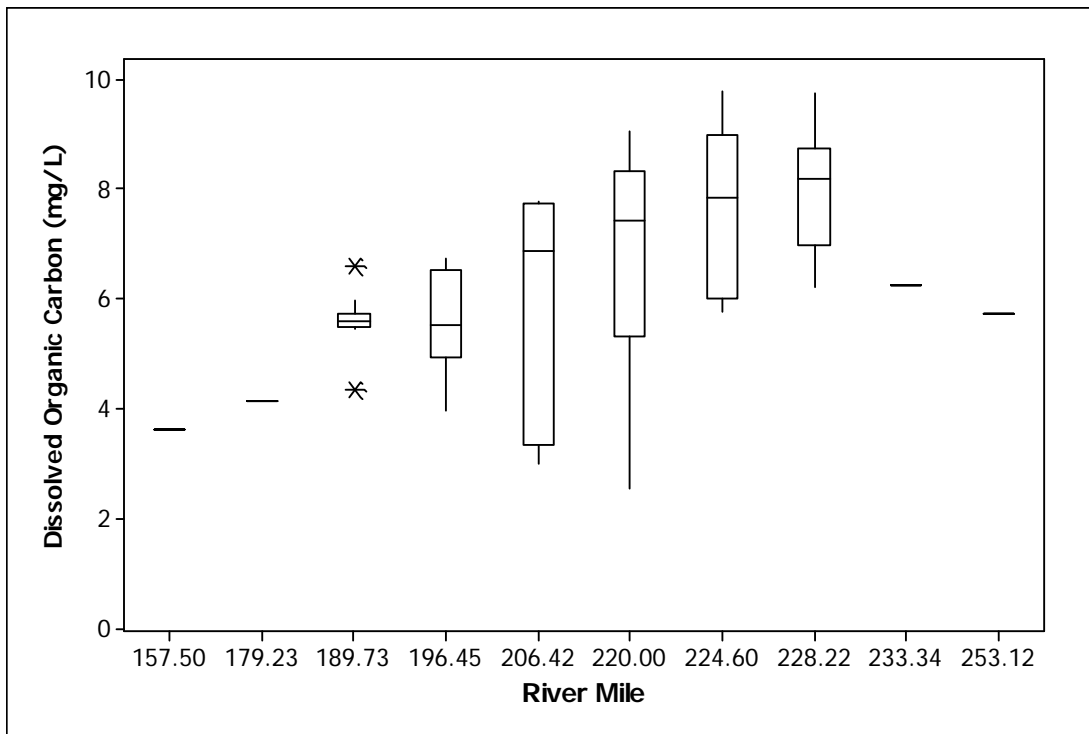


Figure 9. Dissolved organic carbon values measured at various sites in the Klamath River in 2009, plotted against river mile.

Particulate Carbon

Particulate carbon was added to the constituents measured in 2009. Arrangements with the laboratory for shipping samples and supplies, plus some lost samples while field personnel mastered proper procedures, resulted in an incomplete record for 2009. The values obtained for 2009 ranged from a maximum of 2.75 mg/L in the Klamath River above Shovel Creek (KR20642) on May 23 to a minimum of 0.31 mg/L above Iron Gate reservoir (KR19645) on November 17. The overall average for particulate carbon was 1.00 mg/L. Based on the available data, particulate carbon concentration did not appear to differ among the sites (Figure 10). Values appeared to be at a maximum in early summer and decreased to low values in fall and winter.

Suspended Solids

Total suspended solids (TSS) values measured in 2009 ranged from 0.4 mg/L to 13.2 mg/L. The lowest value was recorded on September 19th at Spring Island below the J. C. Boyle power plant. This was a time when the flow in the river at that location was primarily from the springs located upstream. The highest value was recorded on May 25th in the Klamath River above J. C. Boyle reservoir (RM 228). In 2009 TSS decreased slightly in the Klamath River from above J. C. Boyle reservoir to below Iron Gate dam (Figure 11). There was a peak in TSS at most locations in May followed by a decrease to lower, but variable, values that persisted through the summer.

Volatile suspended solids values were low and variable, with no discernable pattern in either seasonally or spatially. Most of the values measured were at or below the method reporting limit.

River Sites – Nutrients

Samples from the river sites in 2009 were analyzed for several nutrient species including ammonia nitrogen, nitrate+nitrite nitrogen, particulate nitrogen, total nitrogen (persulfate method), orthophosphate phosphorus, and total phosphorus. Summary statistics for those nutrient species at all sites and times are presented in Table 5.

Table 5. Summary statistics for nutrients measured at river sites in the Klamath Hydroelectric Project in 2009.

Constituent ^a	N	Mean	Std. Dev	Minimum	Median	Maximum	MAD ^b
Ammonia N	56	0.157	0.244	0.000	0.100	1.160	0.099
Nitrate+nitrite N	56	0.626	0.369	0.020	0.765	1.550	0.195
Particulate N	27	0.165	0.112	0.041	0.159	0.436	0.083
Total N	56	1.336	0.732	0.120	1.150	3.150	0.430
Orthophosphate P	55	0.135	0.050	0.050	0.120	0.250	0.030
Total P	56	0.164	0.071	0.071	0.150	0.360	0.040

^a Units are mg/L as N or P

^b MAD = Median absolute deviation

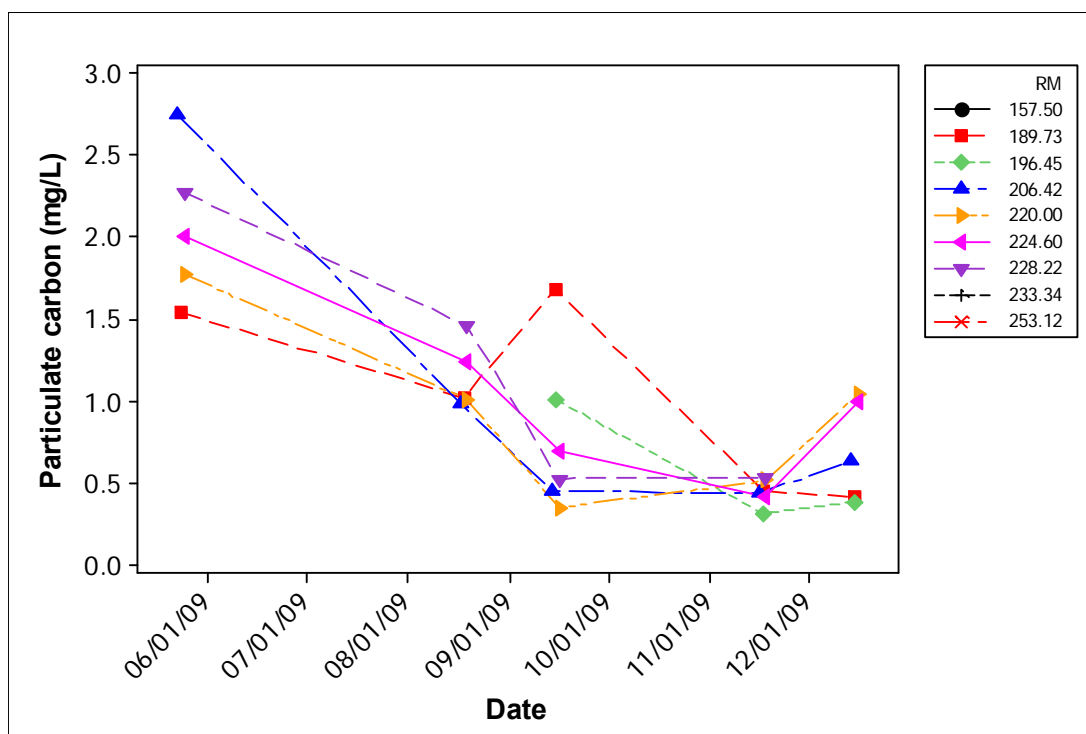
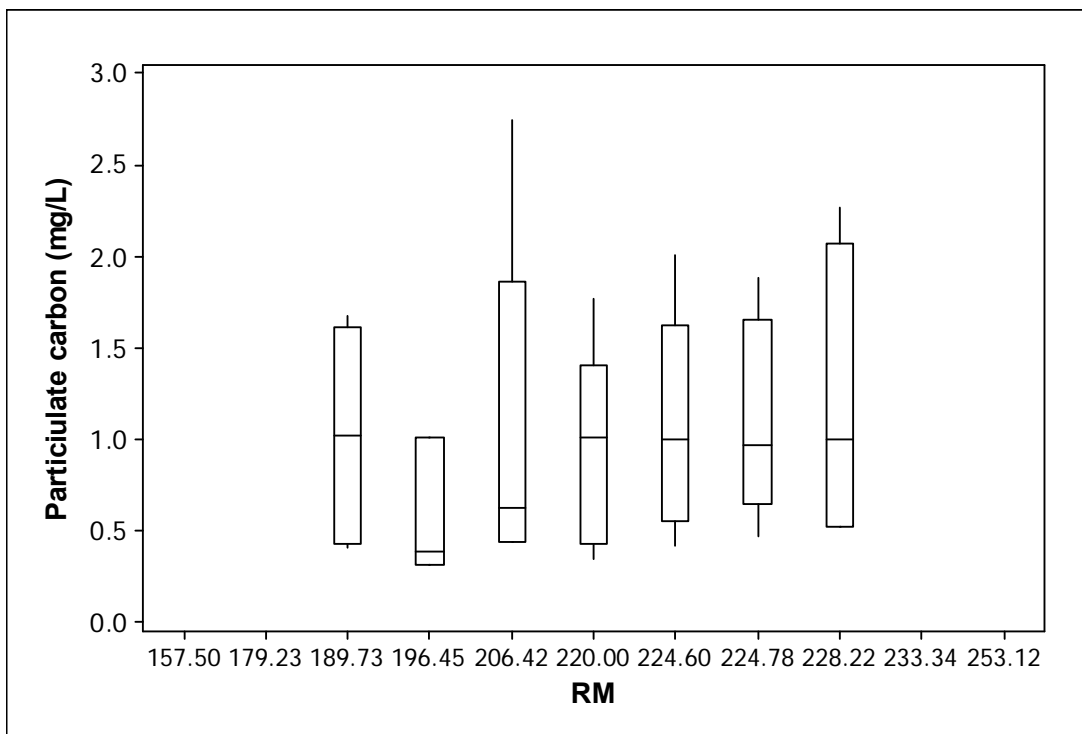


Figure 10. Particulate carbon values measured at various sites in the Klamath River in 2009, plotted against river mile.

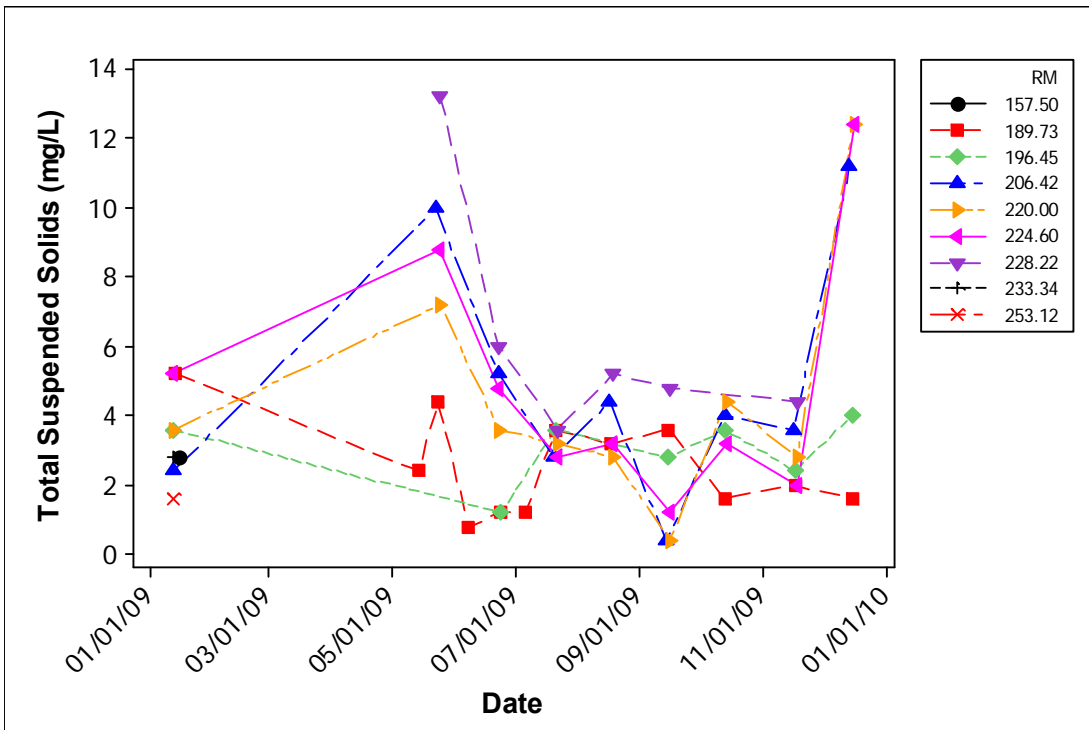
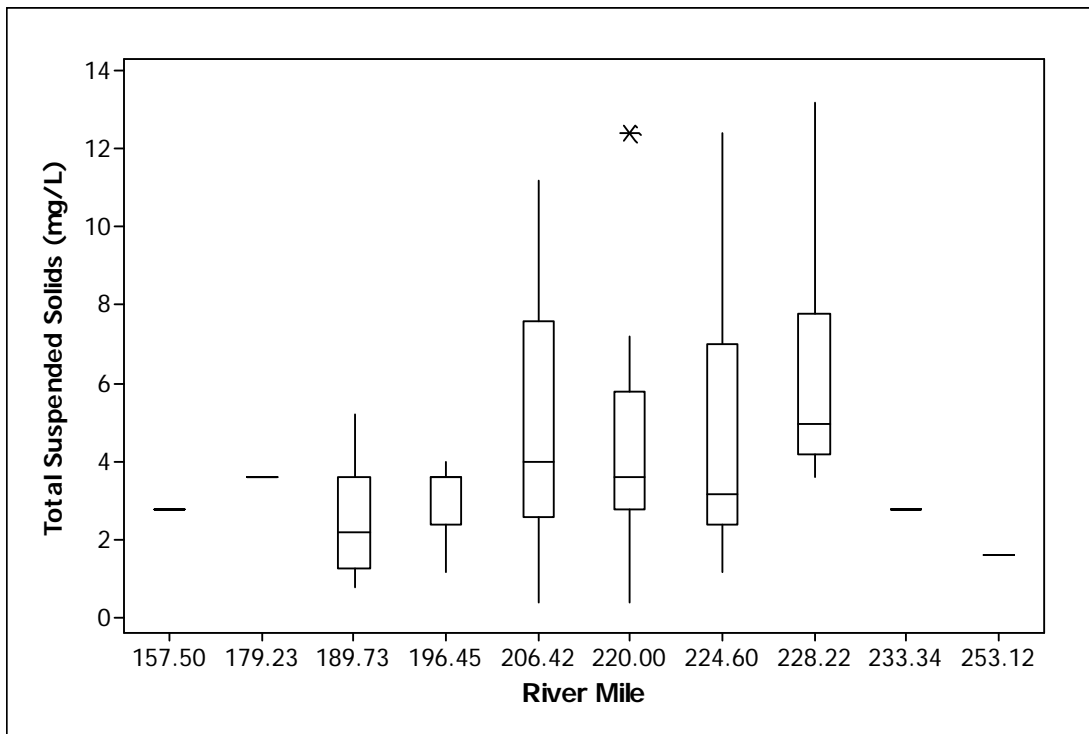


Figure 11. Total suspended solids values measured at various sites in the Klamath River in 2009, plotted against river mile.

Ammonia Nitrogen

Ammonia nitrogen (NH₃) ranged from non-detect to 1.16 mg/L (as N). The lowest value was recorded on May 19th at the site above J. C. Boyle reservoir (RM 228). The highest value was recorded on January 9th at the mouth of Link River (RM 253). The overall average value for NH₃ was 0.16 mg/L. Values for NH₃, shown in Figure 12, were typically higher at sites upstream of the peaking reach below J. C. Boyle dam – river mile 220 and above. NH₃ concentration showed a distinct seasonality with high values in the winter and lower values in the summer. There was a noticeable minimum in May. Many NH₃ values during the summer (May – September) were below the reporting limit for the analytical method. Values from below J. C. Boyle dam were an exception.

Nitrate plus Nitrite Nitrogen

Nitrate plus nitrite nitrogen (NO₃) ranged from 0.02 mg/L (as N) on May 24th below Iron Gate dam (RM 189) to 1.55 mg/L on September 19th above J. C. Boyle reservoir (RM 228). The overall average for NO₃ was 0.63 mg/L. The median concentration of NO₃ below Iron Gate dam was substantially lower than at the sites upstream (Figure 13). Similar to NH₃, NO₃ showed a very low minimum at all locations in May, and then increased to maximum values at most locations in September. Concentrations of NO₃ at the sites below Copco and Iron Gate reservoirs were consistently lower than at other sites.

Particulate Nitrogen

Particulate nitrogen was added to the constituents measured in 2009. Arrangements with the laboratory for shipping samples and supplies, plus some lost samples while field personnel mastered proper procedures, resulted in an incomplete record for 2009. The values obtained ranged from 0.041 mg/L at Spring Island (RM 220) on September 19th, when the river at this site was mostly groundwater, to 0.436 mg/L above Copco reservoir (RM 206) on May 23rd. The overall average for particulate nitrogen was 0.17 mg/L. Based on the available data, particulate nitrogen concentration did not appear to differ among the sites (Figure 14). Values appeared to be lower during the late summer than during winter and spring.

Total Nitrogen

Total nitrogen ranged from 0.12 mg/L (as N) below Iron Gate dam (RM 189) on May 14th to 3.15 mg/L below J. C. Boyle dam on October 14th. The overall average for total nitrogen at the river sites was 1.34 mg/L. Median total nitrogen decreased from above J. C. Boyle reservoir to below Iron Gate dam (Figure 15). The seasonal pattern showed a decrease from intermediate values in January to generally low values in May and June. A general increase in total nitrogen concentration from June to October was interrupted by a decrease at most sites in September.

Phosphorus

Orthophosphate and total phosphorus were similar in concentration at the river sites in 2009, and exhibited similar spatial and temporal patterns. The lowest concentration of orthophosphate, 0.05 mg/L (as P) below J.C. Boyle dam, and of total phosphorus, 0.07 mg/L (as P) above Iron Gate reservoir (RM 196), occurred on December 15th and 16th, respectively. The highest concentration of orthophosphate (0.25 mg/L) occurred below J. C. Boyle dam on September 16th. The highest concentration of total phosphorus (0.36 mg/L) occurred above Iron Gate reservoir on July 21st.

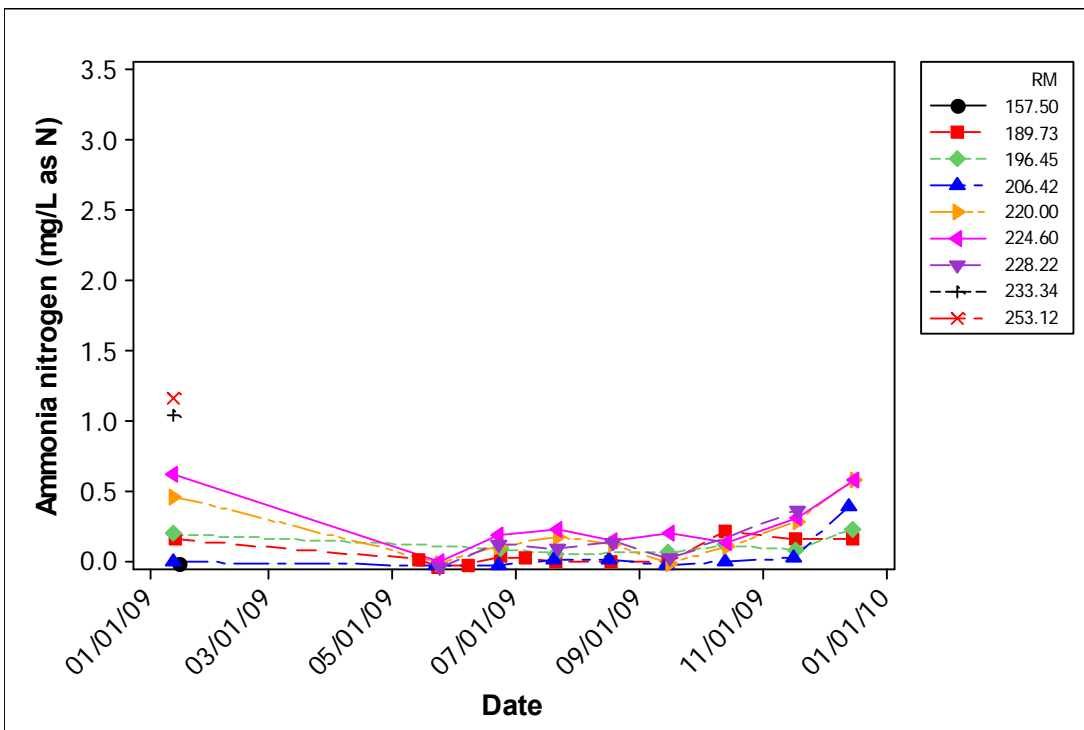
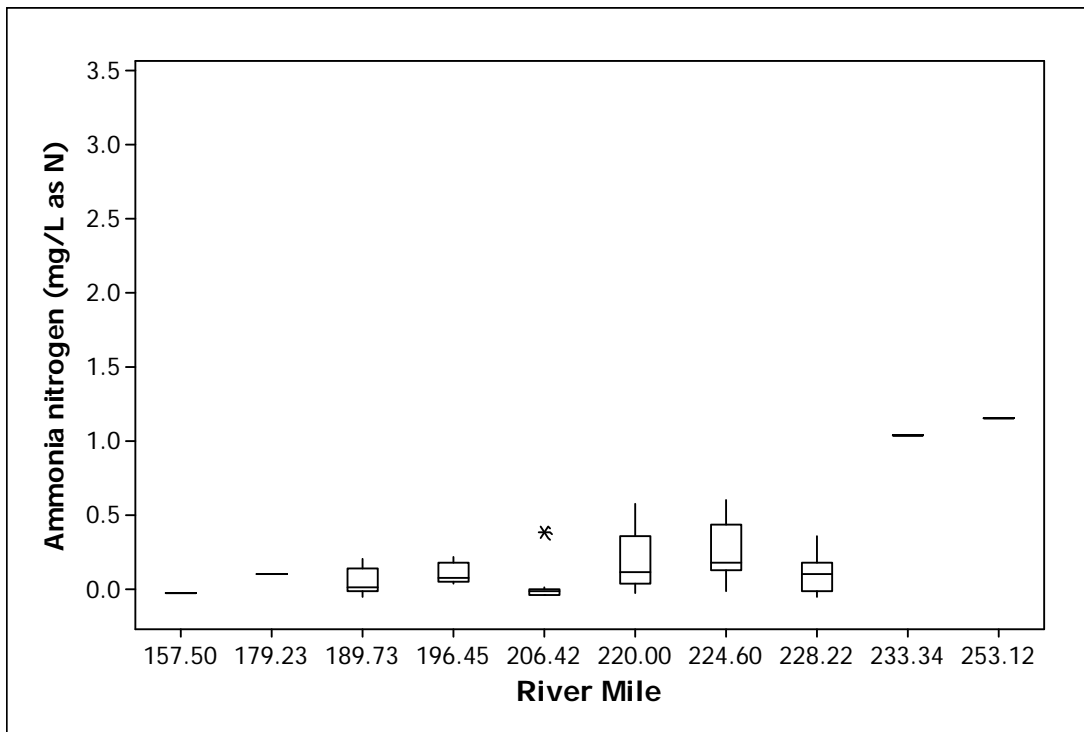


Figure 12. Ammonia nitrogen values measured at various sites in the Klamath River in 2009, plotted against river mile.

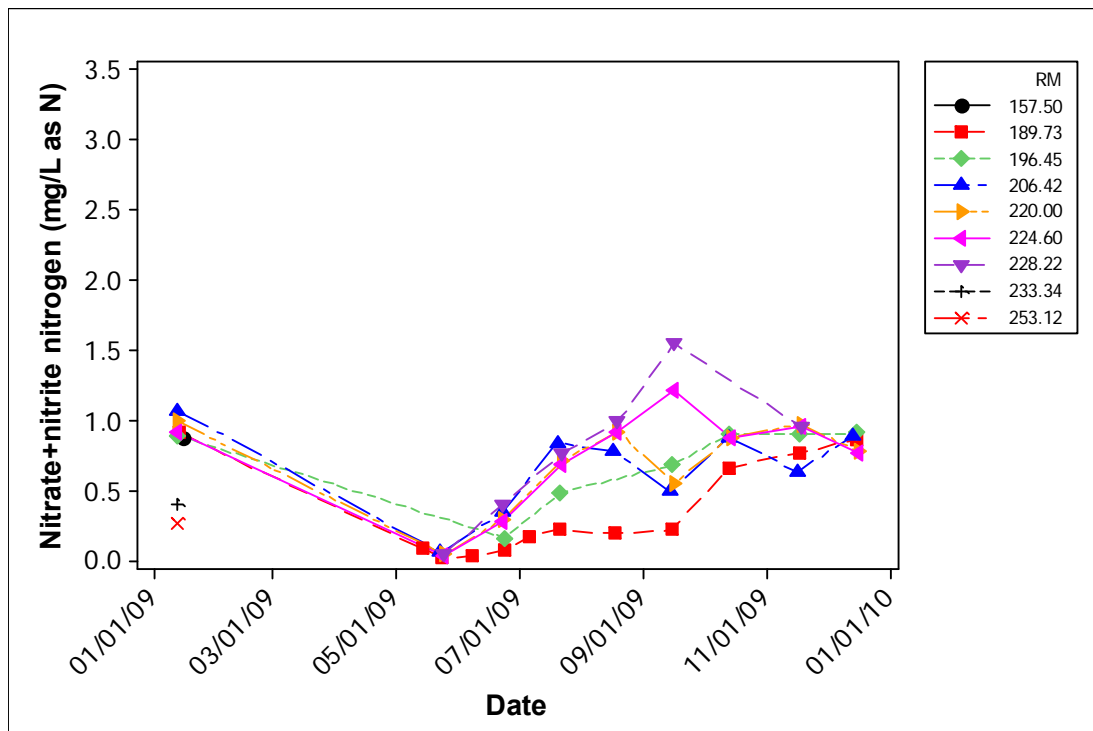
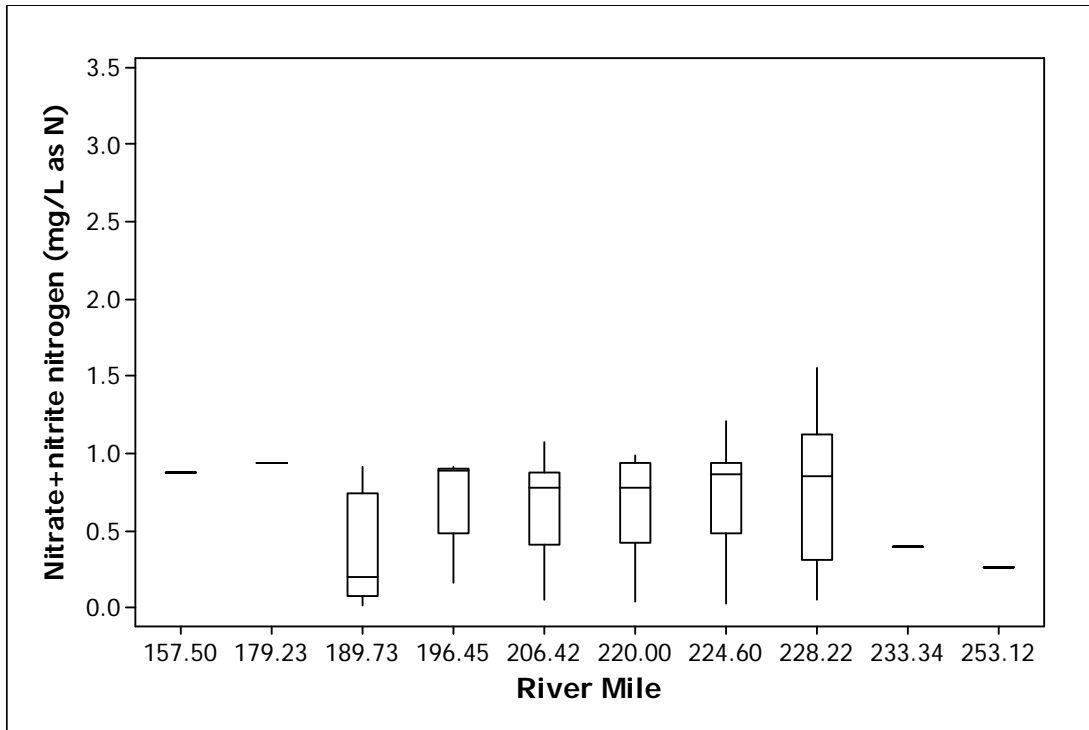


Figure 13. Nitrate + nitrite nitrogen values measured at various sites in the Klamath River in 2009, plotted against river mile.

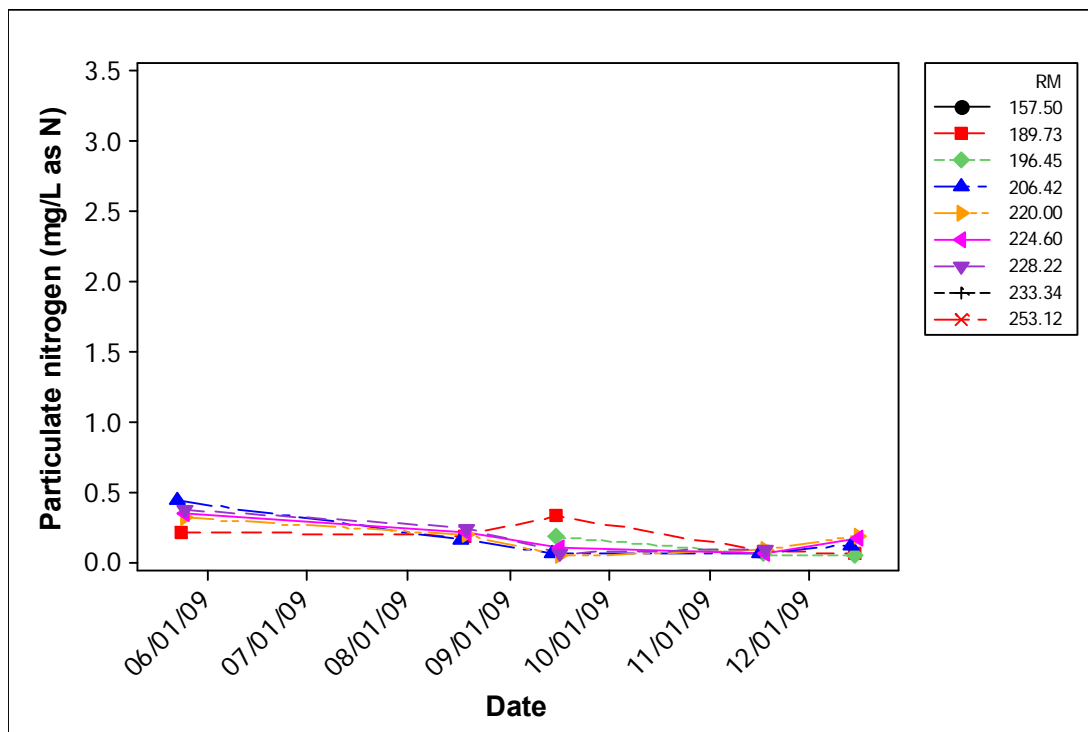
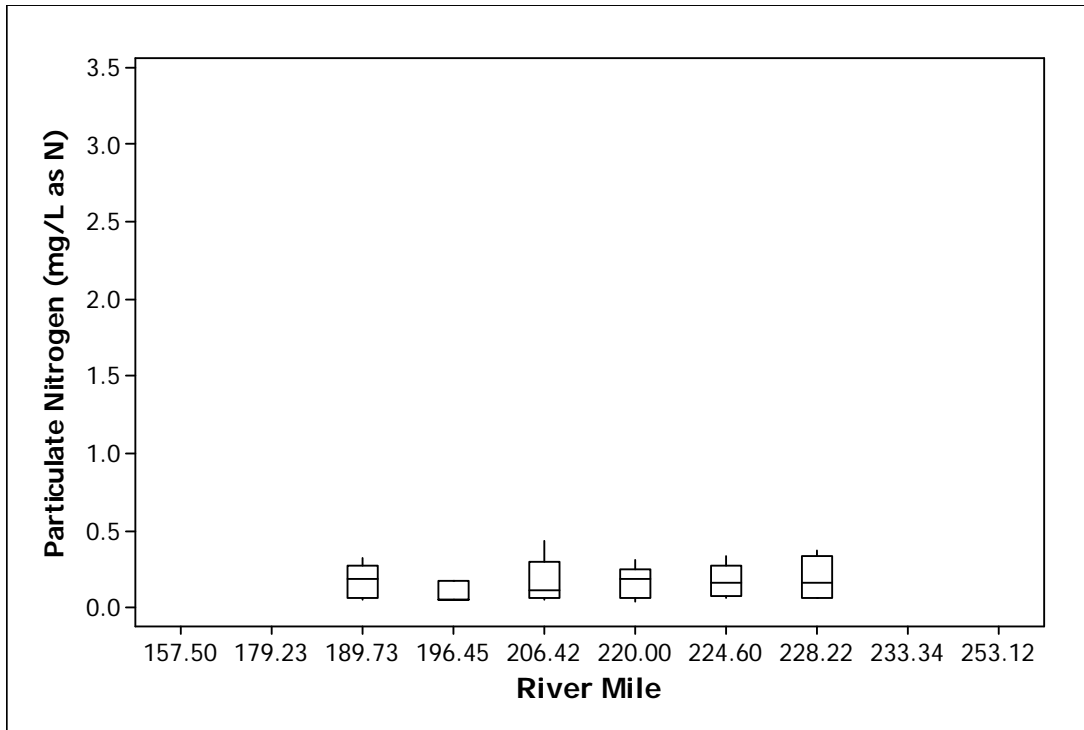


Figure 14. Particulate nitrogen values measured at various sites in the Klamath River in 2009, plotted against river mile.

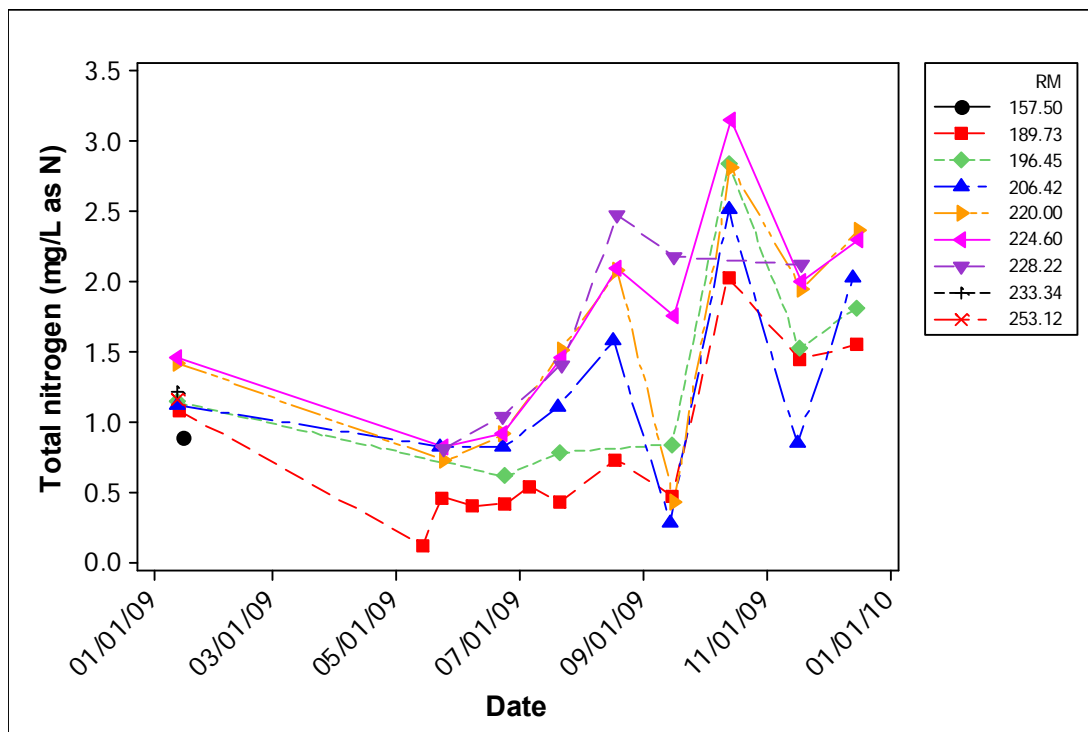
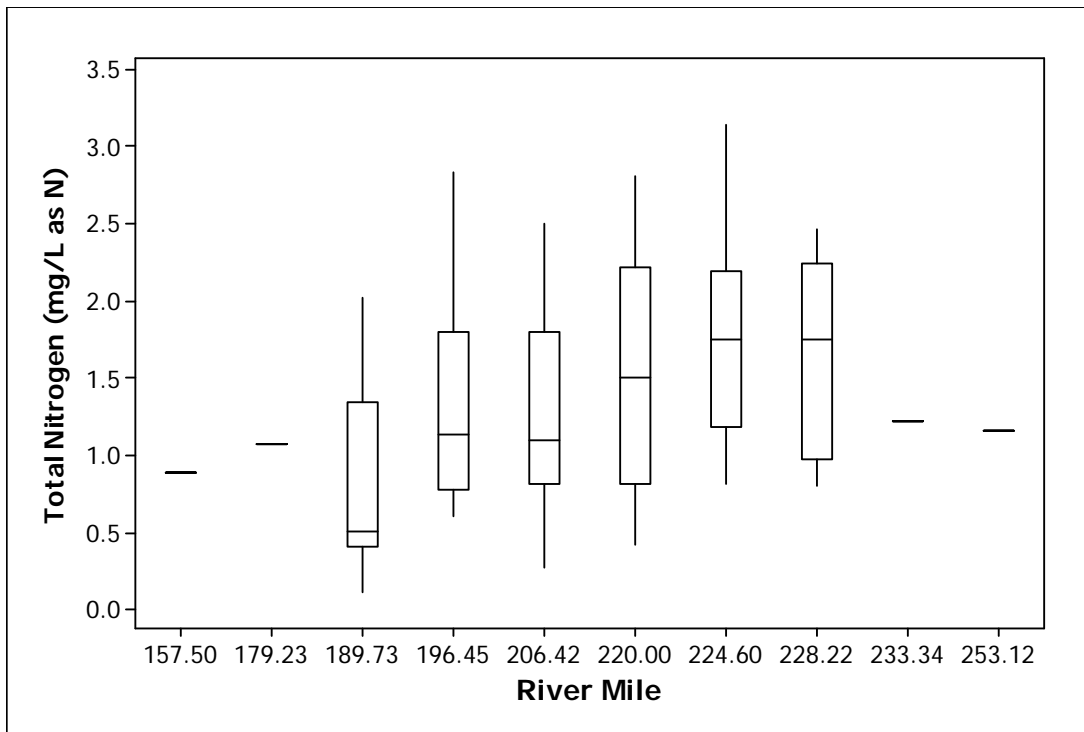


Figure 15. Total nitrogen values measured at various sites in the Klamath River in 2009, plotted against river mile.

The overall average concentration for all river samples was 0.14 mg/L for orthophosphate and 0.16 mg/L to total phosphorus. Median values for orthophosphate and total phosphorus were both lower below Iron Gate reservoir than above J. C. Boyle reservoir. Phosphorus concentration was relatively high from May through October, and lower in the fall and winter. A notable exception occurred in June when both orthophosphate and total phosphorus decreased sharply to wintertime levels. Phosphorus concentration below Iron Gate dam was typically lower than at other upstream locations from January through September. In October through December phosphorus values below Iron Gate dam were higher than at most other locations. Phosphorus data are depicted in Figures 16 and 17.

Reservoir Sites

Measurements of physical variables were made in J. C. Boyle, Copco, and Iron Gate reservoirs in 2009. In each reservoir, *in situ* measurements were made for water temperature, SPC, dissolved oxygen concentration, dissolved oxygen saturation, and pH at intervals from the surface to the bottom; 1 m intervals in J. C. Boyle reservoir, 2 m in Copco reservoir, and 3 m in Iron Gate reservoir. Measurements were made at the log boom or cable line near the dam at approximately the deepest point in the reservoir. Water samples were also collected at this location from various depths in each reservoir (0.5 and 8 m in J. C. Boyle reservoir, 0.5, 9, 18, and 27 m in Copco reservoir, and 0.5, 10, 20, 30, and 40 m in Iron Gate reservoir) and analyzed for water chemistry constituents (i.e., nutrients, suspended solids, and dissolved organic carbon). Results from each reservoir are presented in the following sections.

J. C. Boyle Reservoir

Physical Conditions

Results of vertical profile measurements in J. C. Boyle reservoir are presented in Figure 18. J. C. Boyle reservoir has a short residence time, on the order of hours, and is typically well-mixed vertically. This well-mixed condition was reflected in 2009 in the vertical uniformity of the SPC profiles. SPC values were generally in the range of 145-205 $\mu\text{S}/\text{cm}$, with higher values in the early summer. The abrupt change in SPC between June and July from near 200 $\mu\text{S}/\text{cm}$ to near 150 $\mu\text{S}/\text{cm}$ suggests that there was a change in the source water entering the reservoir.

A similar pattern was observed in temperature values with generally uniform temperatures vertically that change from one sampling period to the next. Temperatures ranged from a high of near 25 °C in July to a low of around 4 °C in November. J. C. Boyle reservoir was not sampled in January or December 2009 because the surface was frozen. Although J. C. Boyle reservoir does not stratify in the classical sense of a temperature driven density gradient that isolates the deeper water from contact with the atmosphere, a relatively small temperature gradient of 1-3 °C persisted from mid June through mid August. This gradient may result from density-driven interflow of Klamath River water at different depths through the reservoir as a result of the diurnal fluctuation in river water temperature.

Dissolved oxygen concentration often decreases with depth in J. C. Boyle reservoir, especially during the summer, a result of the high oxygen demand of the inflow from the Klamath River. An example of the effect of that oxygen demand can be seen in the dissolved oxygen profiles in May, June, and July. The combination of the high oxygen demand and the resistance to vertical

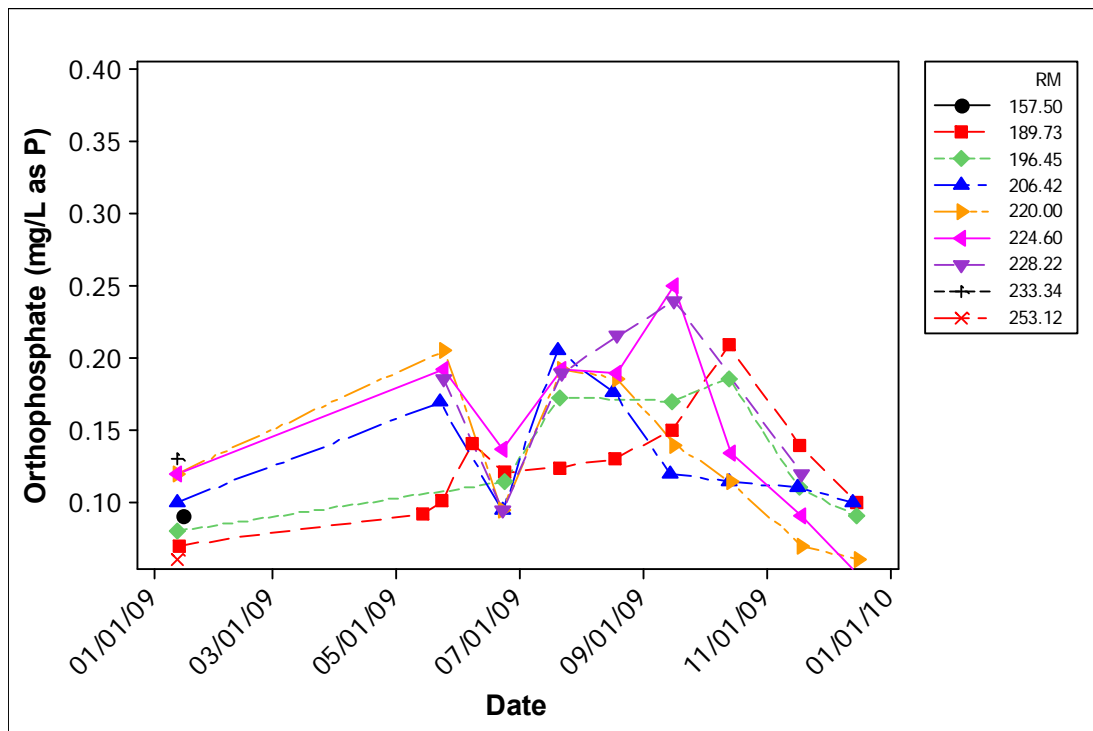
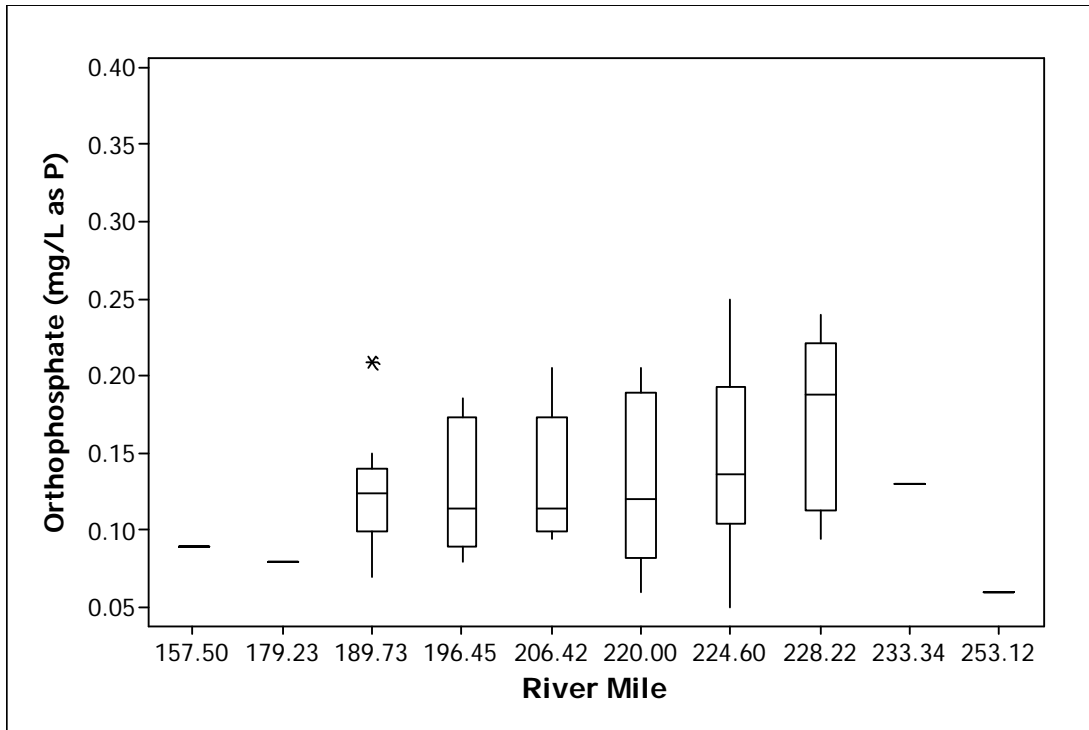


Figure 16. Orthophosphate values measured at various sites in the Klamath River in 2009, plotted against river mile.

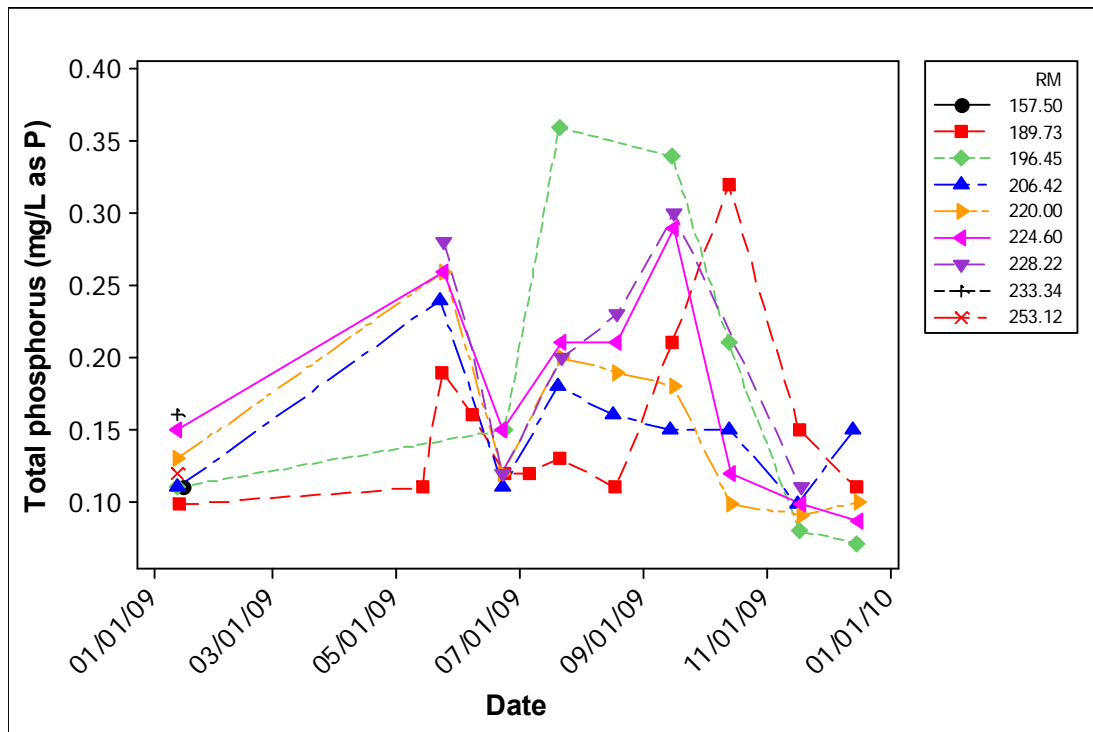
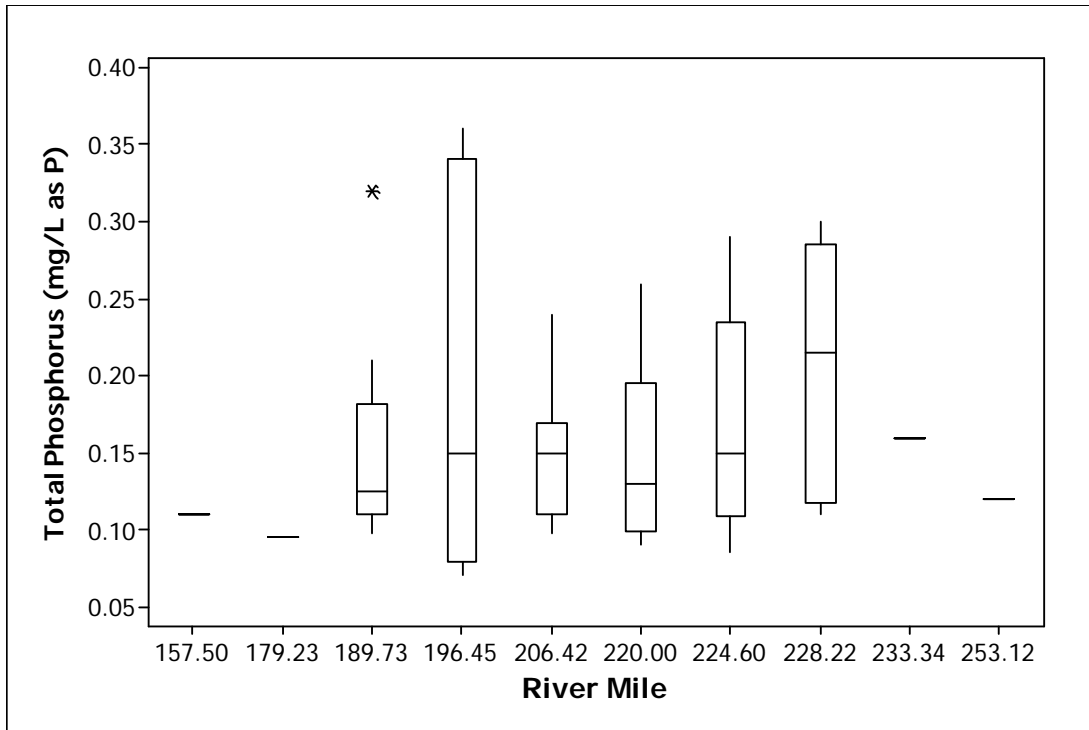


Figure 17. Total phosphorus values measured at various sites in the Klamath River in 2009, plotted against river mile.

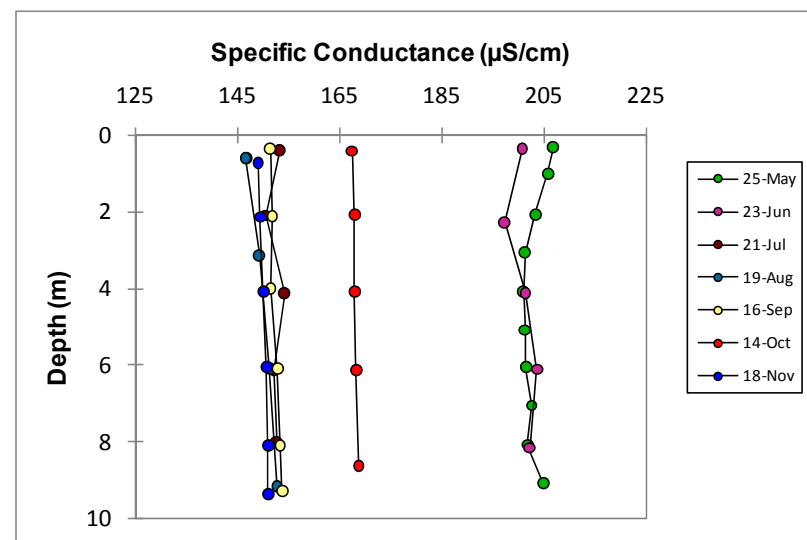
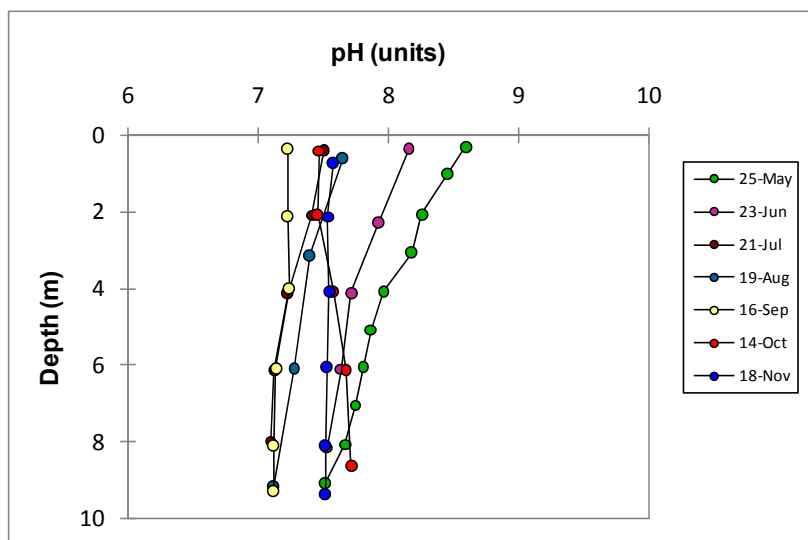
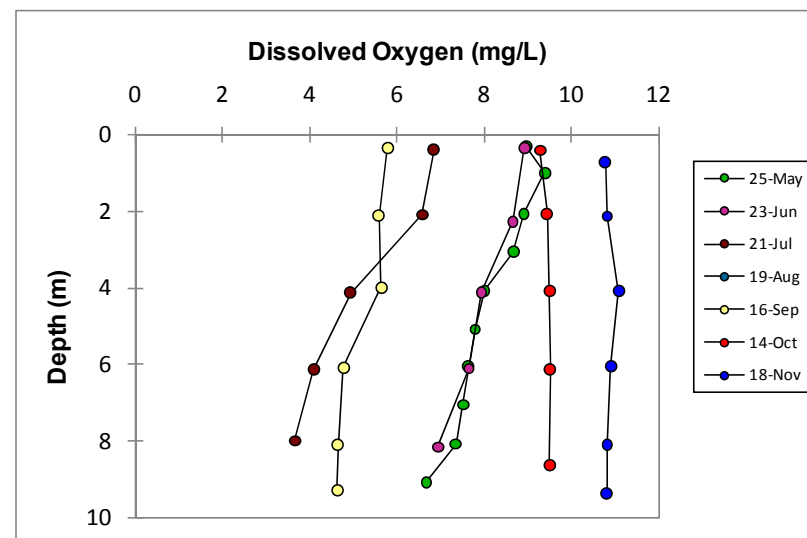
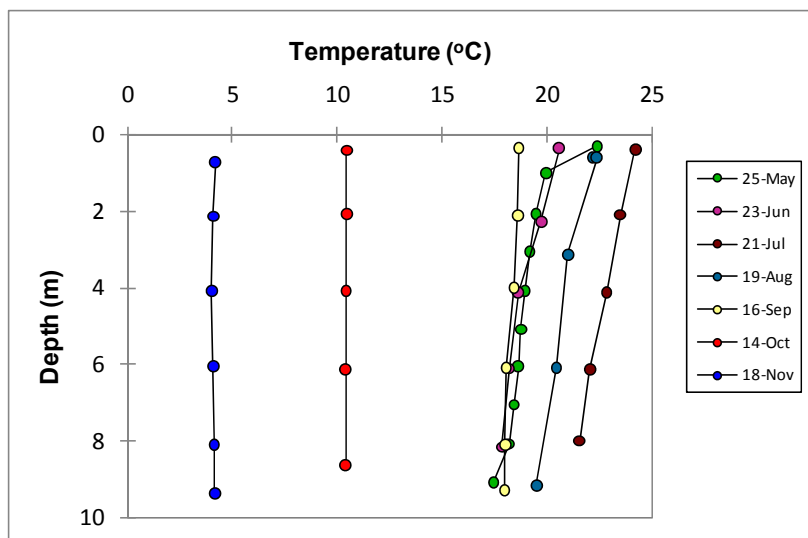


Figure 18. The results of vertical profile measurements for temperature, dissolved oxygen, pH, and specific conductance in J. C. Boyle reservoir in 2009.

mixing imposed by the summertime temperature gradient resulted in a vertical gradient in dissolved oxygen that persisted from May into mid September. Dissolved oxygen concentration at depth ranged from near 3 mg/L in July to more than 10 mg/L in November.

Values of pH exhibited a vertical gradient in May and June, decreasing with depth. From July 15 through November, pH values generally ranged between 7.1 and 7.7 at all depths. Surface values of pH exceeded 8.0 in May and June, and exceeded 8.5 in May.

Nutrients

Nutrients (N and P) were measured on samples collected from J. C. Boyle reservoir in May through November at 0.5 m and 8 m depth. The results of nutrient analysis are depicted in Figure 19. Inorganic nitrogen – primarily nitrate – concentration in J. C. Boyle reservoir increased steadily from May through September, then fluctuated at somewhat lower concentration in October and November. There was little difference in concentration between 0.5 m and 8 m. Total nitrogen followed a similar pattern, but reached its maximum concentration in October, rather than September.

Orthophosphate P concentration typically ranged between 0.20 to 0.25 mg/L except in June, October, and November when values were considerably lower. Peak concentration was observed in September. Total phosphorus followed a similar pattern. The seasonal pattern of nutrients in J. C. Boyle reservoir follows the pattern seen in the Klamath River above J. C. Boyle reservoir.

Summary statistics for the nutrients measured in J. C. Boyle reservoir are provided in Table 6.

Table 6. Summary statistics for nutrients measured in J. C. Boyle reservoir in 2009.						
Descriptive Statistics for Depth = 0.5 m						
	NH3	NO3	TIN	NT	PO4	PT
N	7	7	7	7	7	7
Mean	0.176	0.665	0.841	1.644	0.153	0.199
Std. Dev.	0.140	0.404	0.495	0.756	0.064	0.082
Minimum	0.00	0.00	0.00	0.69	0.08	0.1
Median	0.15	0.85	1	1.52	0.18	0.18
Maximum	0.36	1.12	1.28	2.9	0.22	0.31
MAD	0.03	0.22	0.28	0.51	0.04	0.06
Descriptive Statistics for Depth = 8 m						
	NH3	NO3	TIN	NT	PO4	PT
N	7	7	7	7	7	7
Mean	0.205	0.683	0.888	1.650	0.164	0.216
Std. Dev.	0.105	0.392	0.477	0.661	0.061	0.082
Minimum	0.014	0.05	0.064	0.79	0.1	0.094
Median	0.21	0.84	1.01	1.71	0.18	0.21
Maximum	0.34	1.16	1.46	2.62	0.25	0.35
MAD	0.04	0.18	0.26	0.39	0.07	0.06

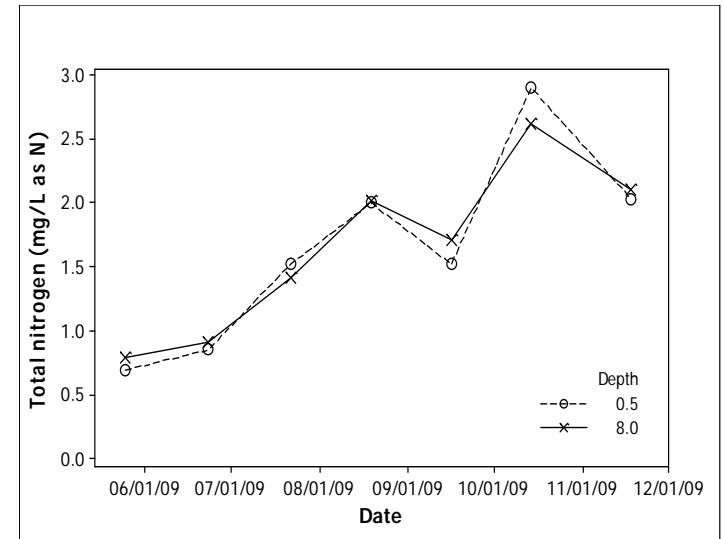
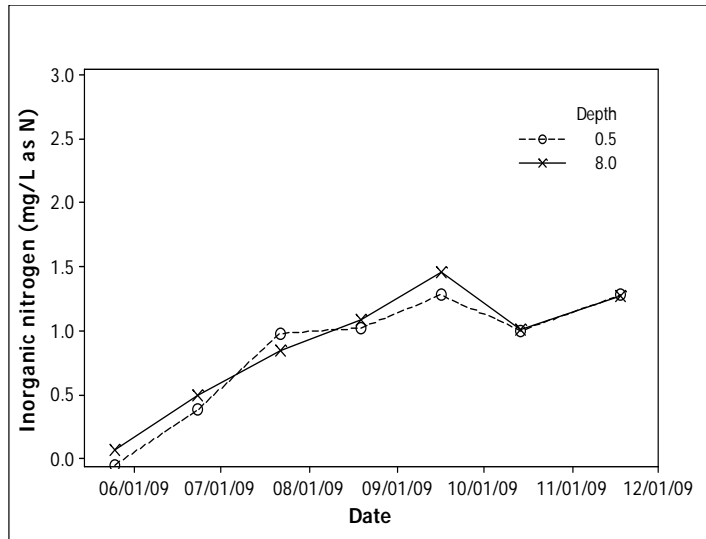
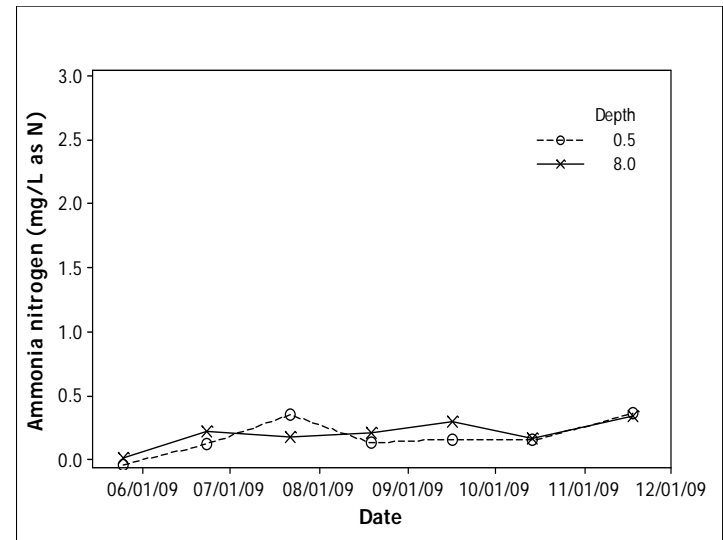
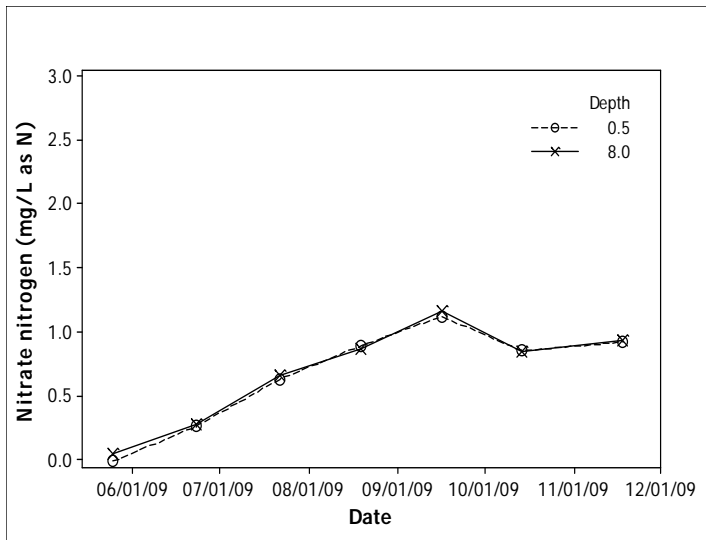


Figure 19. The results of analysis for nitrogen and phosphorus of water samples collected at 0.5 m and 8 m depths in J. C. Boyle reservoir in 2009.

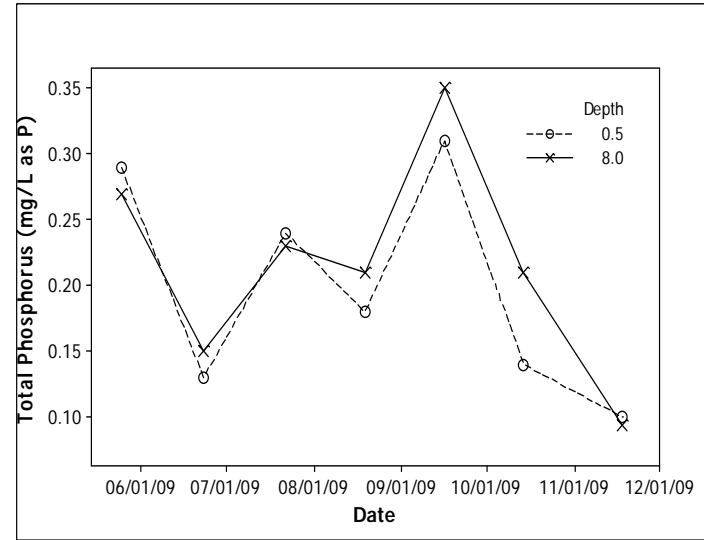
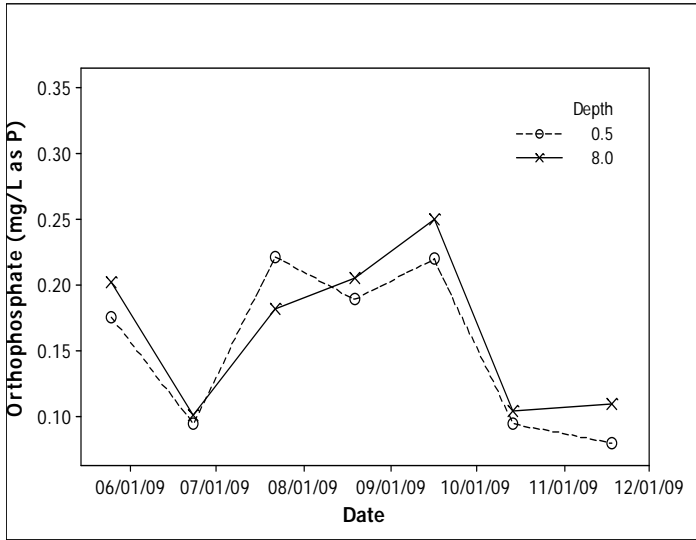


Figure 19. Continued.

Other Constituents

The results of analysis for total alkalinity, suspended solids, and dissolved organic carbon are presented in Figure 20. Total alkalinity changed sharply between June and July, echoing a similar change in SPC, again suggesting a change in the source water. There was little difference in alkalinity between 0.5 m and 8 m. In contrast, there was a noticeable difference between 0.5 m and 8 m in the concentration of suspended solids. The reduction in current velocity in the reservoir may have allowed suspended matter to settle toward the bottom. Dissolved organic carbon concentration was similar between 0.5 m and 8 m with the exception of the September measurement. The September peak at 0.5 m depth in J. C. Boyle reservoir reflects a similar September peak at the site above J. C. Boyle reservoir.

Copco Reservoir

Measurements of physical constituents (temperature, specific conductance, pH and dissolved oxygen) were made at 2 m intervals in Copco reservoir in January and May through December in 2009. Additional samples for laboratory analysis were collected at 0.5, 9, 18, and 27 m depths. Results of the profile measurements are presented in Figure 21.

Physical Conditions

Temperature

The seasonal temperature profile in Copco reservoir in 2009 was similar to prior years. The reservoir was isothermal in January, and a vertical temperature gradient had already formed by May when the reservoir was sampled next. The metalimnion, a region of rapid vertical temperature change, was established by June that extended from about 18 to 22 m. Below that the hypolimnion remained isothermal at approximately 11 °C. Thermal stratification had nearly disappeared by mid October. There was evidence of inverse stratification in December. The epilimnion, from 0 to about 11 m depth was largely isothermal, but showed evidence of surface heating and a resulting thermal gradient throughout the summer. Maximum surface temperature of nearly 25 °C was observed in July.

Specific Conductance

The seasonal pattern of specific conductance (SPC) was complex, but similar to prior years. SPC changed substantially between sampling events ranging from near 180 $\mu\text{S}/\text{cm}$ in January to more than 200 $\mu\text{S}/\text{cm}$ in May and June, then decreasing to near 160 $\mu\text{S}/\text{cm}$ in July and August apparently in response to changing conditions of the source water from upstream. Such changes affected the entire reservoir only during the isothermal winter period, however. During the summer stratification the SPC values in the hypolimnion were nearly constant at approximately 235 $\mu\text{S}/\text{cm}$.

Dissolved Oxygen

Dissolved oxygen in Copco reservoir in 2009 followed a typical clinograde vertical profile with oxygen depleted in the hypolimnion during the period of stratification. Dissolved oxygen concentration was near 100 percent saturation and uniform with depth in January. By May, however, dissolved oxygen was depleted in the hypolimnion below about 20 m. Photosynthetic activity in the epilimnion kept dissolved oxygen concentration near the surface at high levels

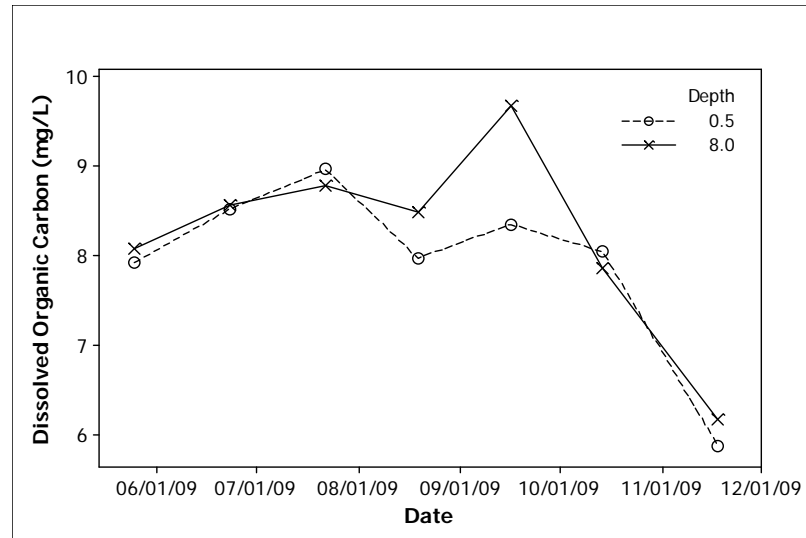
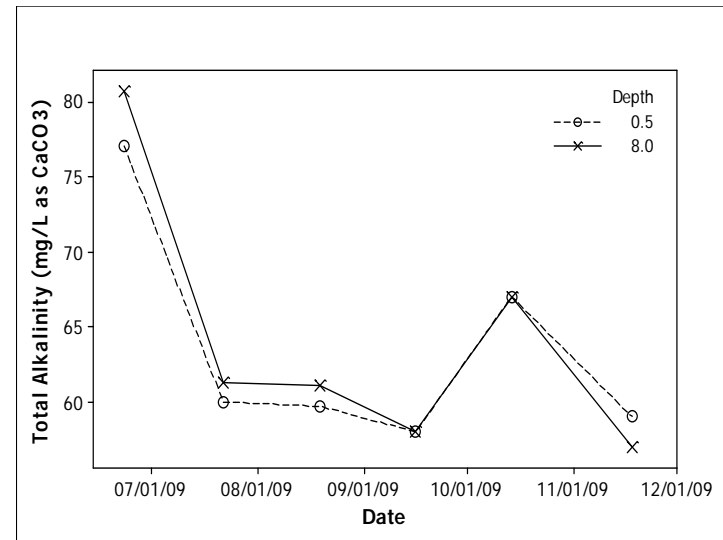
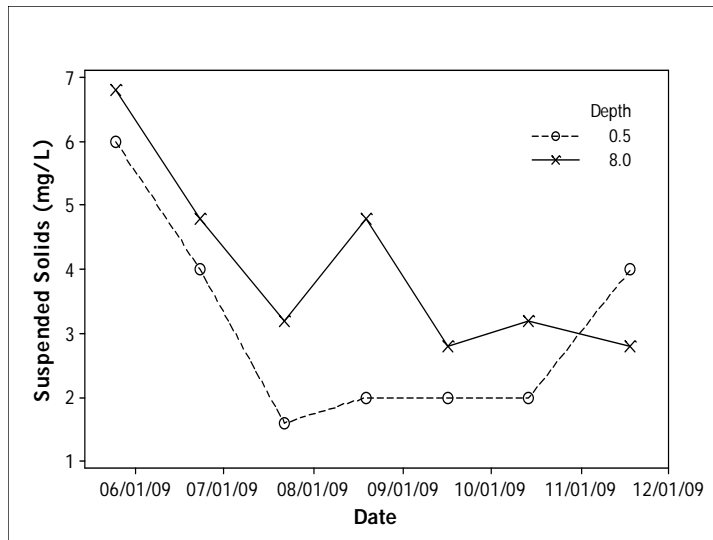


Figure 20. The results of analysis for total suspended solids, total alkalinity, and dissolved organic carbon, of water samples collected at 0.5 m and 8 m depths in J. C. Boyle reservoir in 2009.

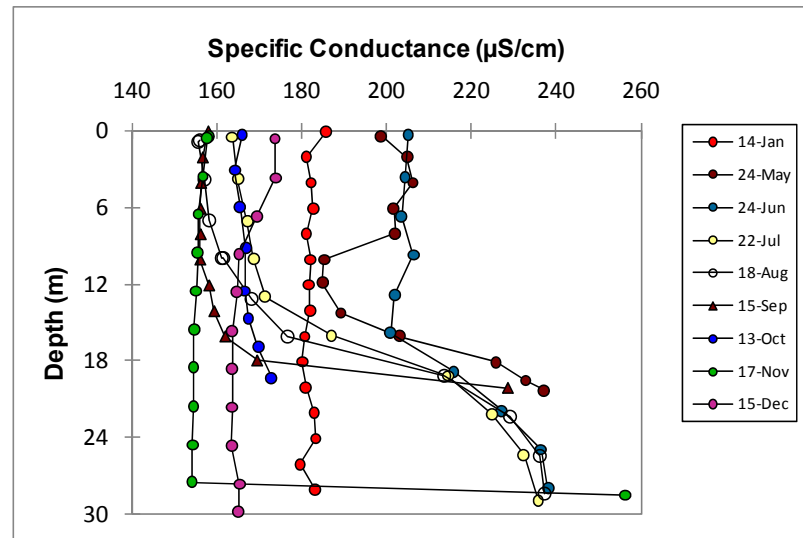
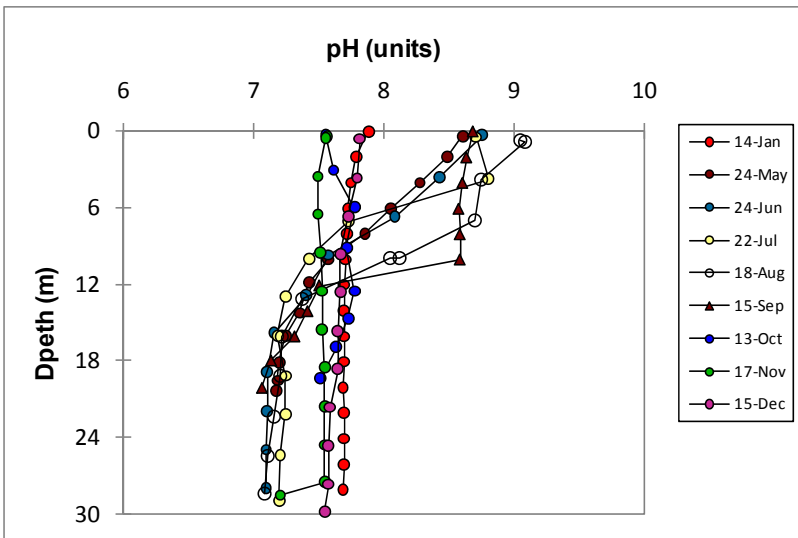
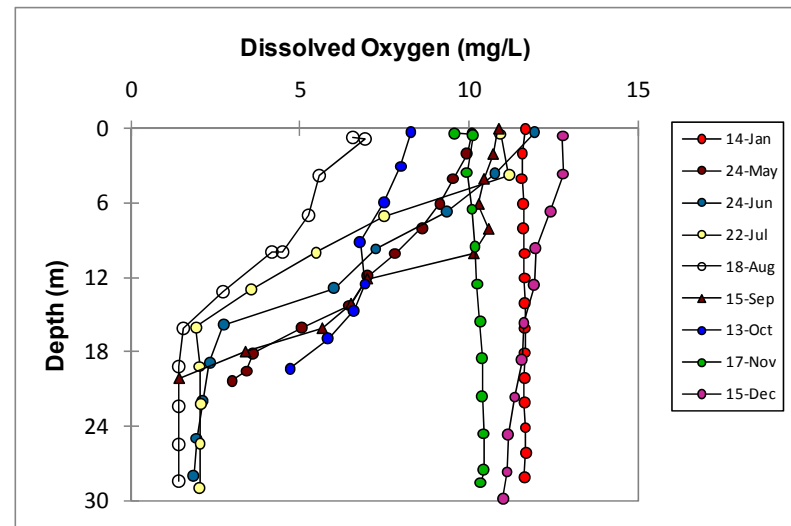
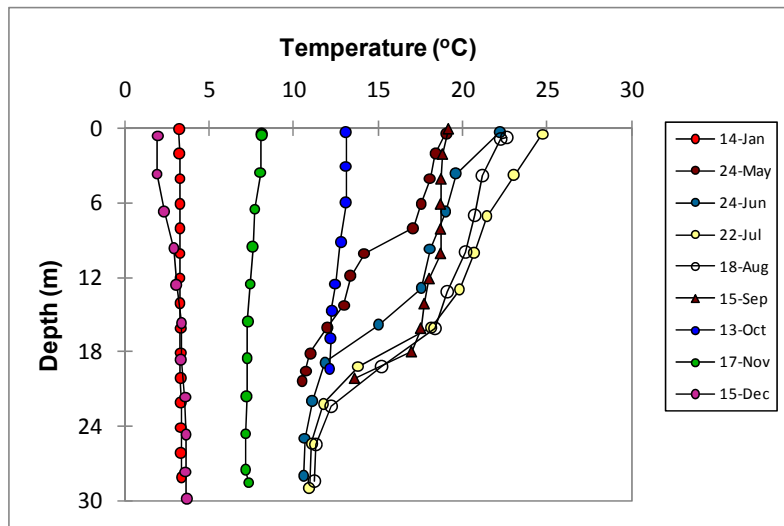


Figure 21. The results of vertical profile measurements for temperature, dissolved oxygen, pH, and specific conductance in Copco reservoir in 2009.

during the summer, with the exception of August, while the depth of the anoxic zone rose to approximately 15 m. By mid-November dissolved oxygen concentration was again near 100 percent saturation and uniform with depth.

pH

During the isothermal period pH in Copco reservoir ranged between 7.7 to 7.9 over the depth of the reservoir. During the period of stratification surface pH was typically about 8.6, although it exceeded 9.1 in August, while pH in the hypolimnion remained near 7.2. The gradual change in pH (and temperature) with depth in the epilimnion in May and June suggests that there was not much mixing in the surface zone during this period. As mixing in the epilimnion increased in August and September, pH in the top 10 m of Copco reservoir became more uniform with depth.

Nutrients

Summary statistics for nutrient data from Copco reservoir are provided in Table 7. Nutrient data from Copco reservoir measured in 2009 are presented in Figure 22. Winter nitrogen concentration in Copco reservoir was uniform with depth at approximately 1 mg/L as N. In May nitrogen values were uniform with depth and near the reporting limit of the analytical method. From May through October nitrogen values varied with depth and by the nitrogen compound. Nitrate nitrogen generally increased through the season at all depths except at 27 m where the concentration stayed near the analytical limits through September. Increases in NO₃ at depth after September brought the concentration to a uniform concentration near 1 mg/L as N by November, when the reservoir was again isothermal. In contrast, ammonia nitrogen (NH₃) concentrations in the stayed low and relatively constant throughout the summer with the exception of samples at 18 and 27 m. Concentrations at 18 m were somewhat elevated throughout the summer, relative to shallower samples, and concentrations at 27 m showed a marked increase during the period of hypolimnetic anoxia.

It can be observed in Figure 22 that on occasion the value for inorganic nitrogen on a specific date and sample is greater than the value for total nitrogen. This is the result of an unexpected incompatibility between the analytical method and the field method of sample preservation. When the problem was discovered steps were taken to correct the problem (See the Appendix). Because of this difficulty it is inappropriate to compare the results for total nitrogen to other analyses, but the total nitrogen results appear to be internally consistent, and may be compared to one another.

The pattern of seasonal changes in phosphorus concentrations was generally similar to that of NH₃-H with relatively constant concentrations at the shallower depths with slightly elevated concentrations at 18 m and a marked increase at 27 m during the period of hypolimnetic anoxia. These patterns are similar to what has been observed in other years.

Particulates

Copco and Iron Gate reservoirs support dense blooms of cyanobacteria during the late summer. Cyanobacteria are able to regulate their buoyancy and tend to accumulate during the day near the surface of the reservoirs. This habit is reflected in the results of analysis for various forms of particulate matter (Figure 23). Total suspended solids, volatile suspended solids, particulate carbon, and particulate nitrogen all reach a peak in August in the sample taken at 0.5 m depth.

Table 7. Summary statistics for nutrient samples analyzed from Copco reservoir in 2009.

Descriptive Statistics for Depth = 0.5 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.069	0.549	1.274	0.618	0.126	0.165
Std. Dev.	0.106	0.362	0.718	0.446	0.036	0.048
Minimum	0.00	0.00	0.49	0.00	0.08	0.096
Median	0.032	0.59	1.12	0.574	0.12	0.16
Maximum	0.28	0.88	2.74	1.16	0.2	0.25
MAD	0.05	0.29	0.43	0.406	0.02	0.02

Descriptive Statistics for Depth = 9 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.101	0.575	1.141	0.676	0.139	0.142
Std. Dev.	0.086	0.345	0.657	0.403	0.042	0.037
Minimum	5.00E-03	0.00	0.51	3.70E-03	0.09	0.095
Median	0.11	0.6	0.99	0.611	0.14	0.15
Maximum	0.26	0.89	2.52	1.15	0.22	0.2
MAD	0.07	0.29	0.37	0.389	0.02	0.04

Descriptive Statistics for Depth = 18 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.260	0.530	1.224	0.790	0.207	0.225
Std. Dev.	0.104	0.403	0.688	0.322	0.081	0.091
Minimum	0.084	0.036	0.45	0.322	0.1	0.092
Median	0.23	0.8	0.99	0.964	0.21	0.27
Maximum	0.41	0.92	2.73	1.12	0.31	0.33
MAD	0.05	0.12	0.34	0.156	0.08	0.02

Descriptive Statistics for Depth = 27 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.796	0.342	1.244	1.138	0.503	0.506
Std. Dev.	0.703	0.433	0.645	0.543	0.445	0.368
Minimum	0.00	0.00	0.52	0.00	0.1	0.11
Median	1	0.016	0.96	1.11	0.5	0.55
Maximum	1.94	0.9	2.68	1.956	1.4	1.11
MAD	0.79	0.029	0.44	0.1192	0.36	0.31

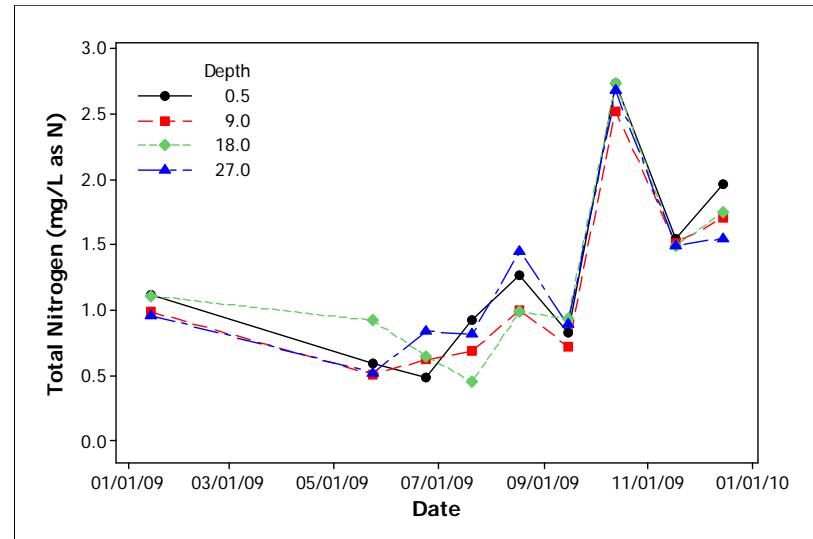
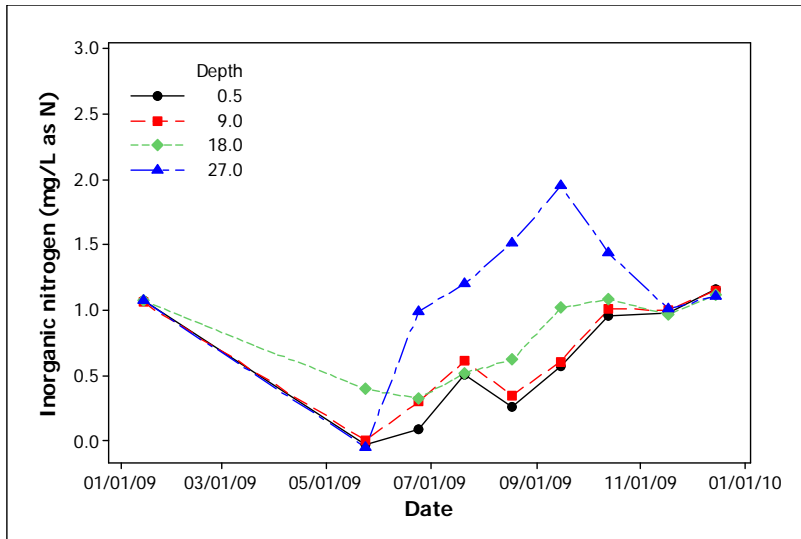
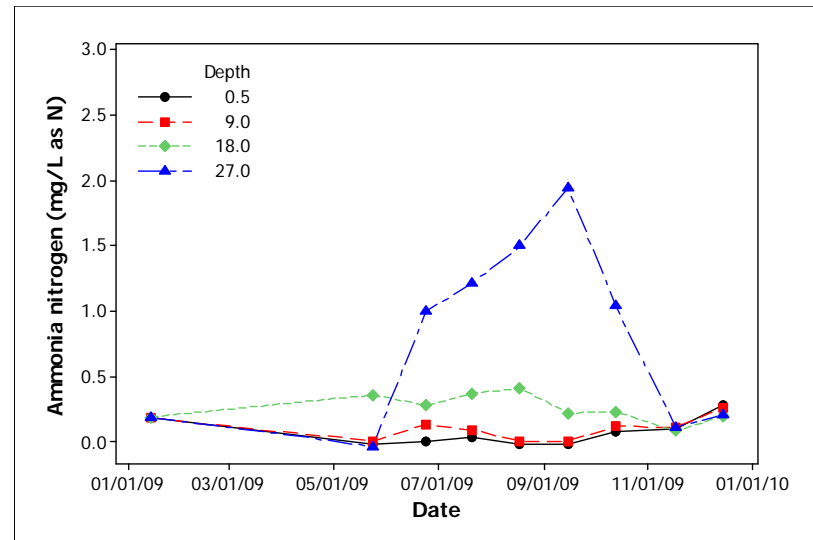
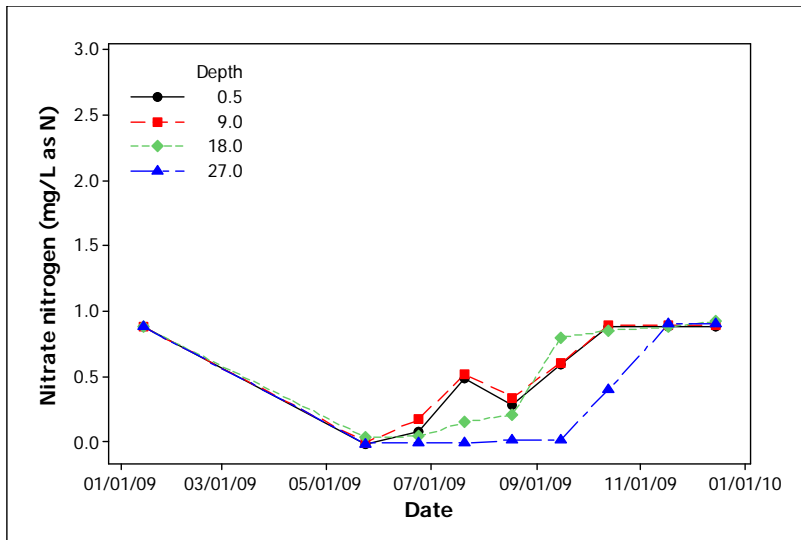


Figure 22. The results of analysis for forms of nitrogen and phosphorus in water samples collected at various depths in Copco reservoir in 2009.

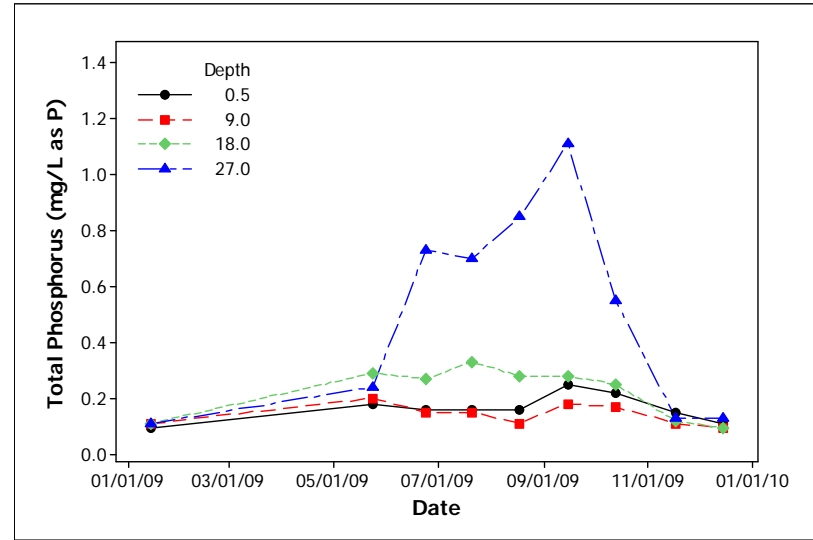
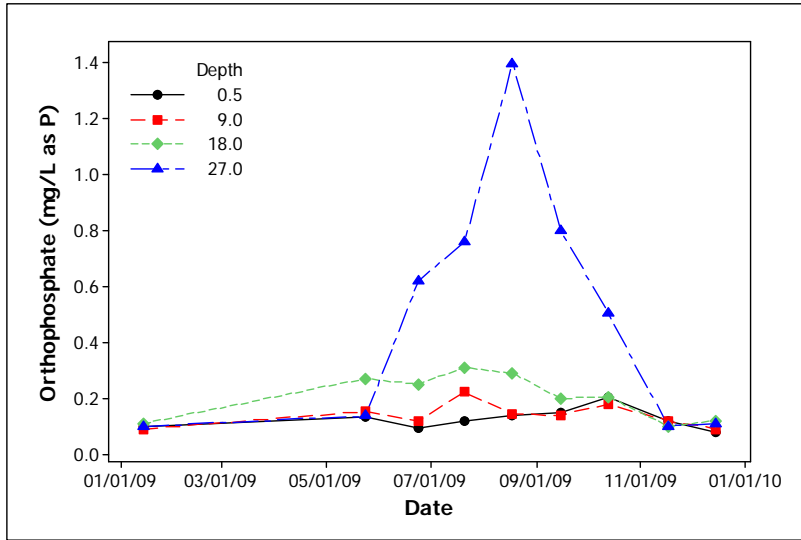


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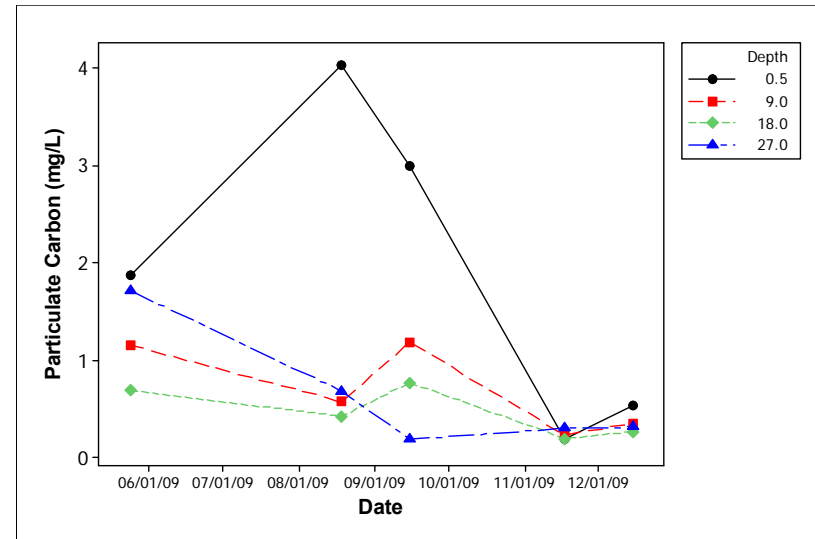
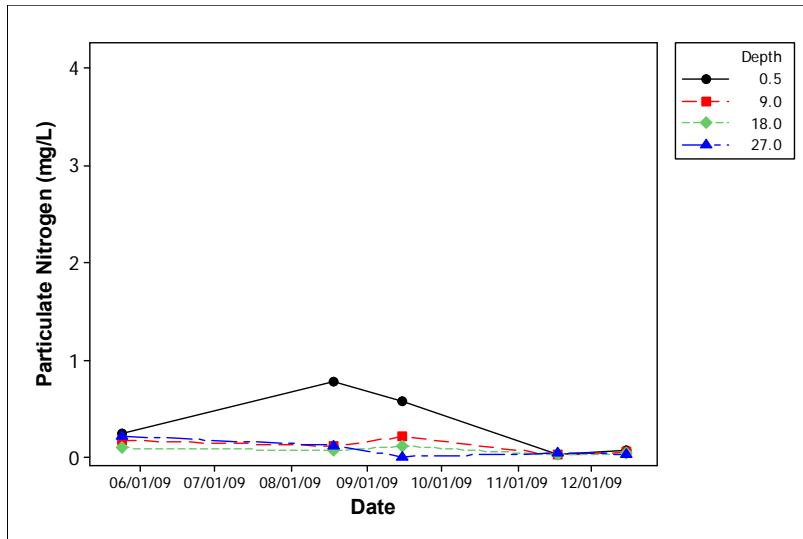
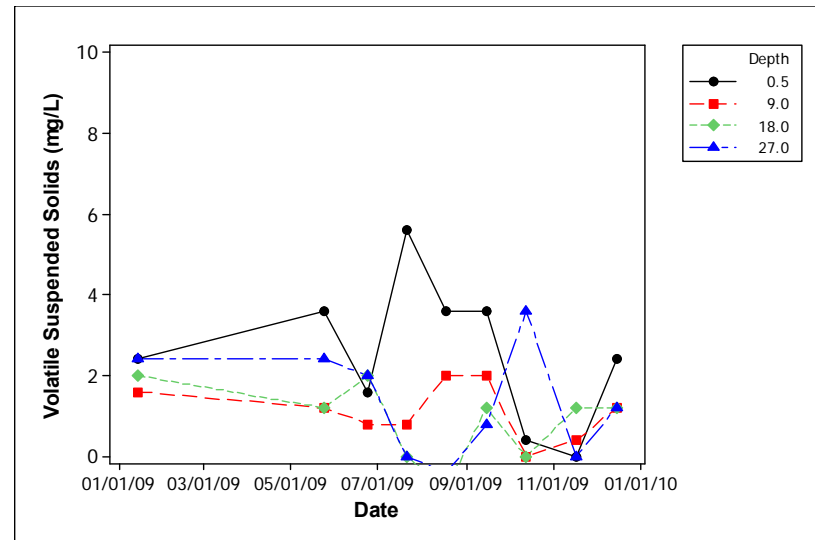
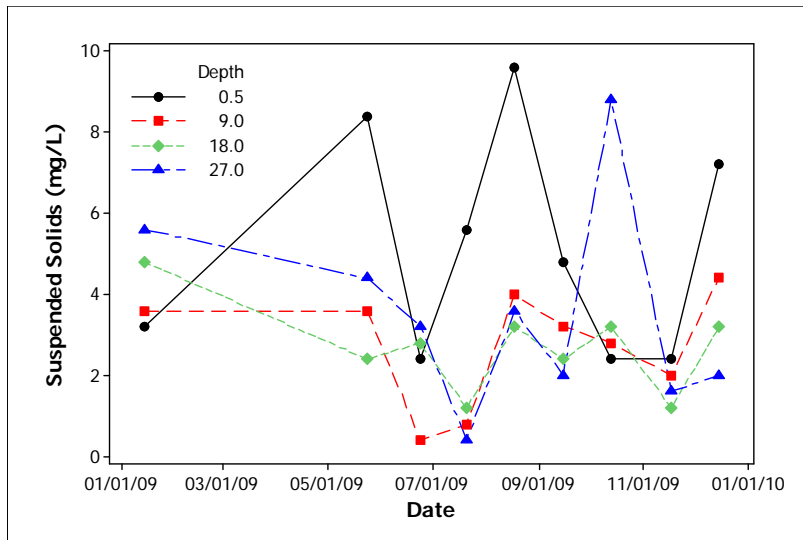


Figure 23. The results of analysis for forms of particulate matter in samples collected at various depths in Copco reservoir in 2009.

Iron Gate Reservoir

Measurements of physical constituents (temperature, specific conductance, pH and dissolved oxygen) were made at 3 m intervals in Iron Gate reservoir in January and May through December in 2009. Additional samples for laboratory analysis were collected at 0.5, 10, 20, 30, and 40 depths.

Physical Conditions

Iron Gate reservoir exhibited seasonal temperature stratification and hypolimnetic oxygen depletion in 2009 as did Copco reservoir, but the details were slightly different. Results of the profile measurements in Iron Gate reservoir are presented in Figure 24. Iron Gate reservoir was still decidedly stratified when sampled in October, and with a slight gradient still evident in November where Copco reservoir was nearly isothermal by October. The hypolimnetic temperature in Iron Gate was cooler (around 8 °C) than the hypolimnion in Copco (11 °C). The metalimnion in both reservoirs extended from approximately 12 to 20 m depth.

Dissolved oxygen, likewise, was vertically uniform in Copco reservoir by November, but still exhibited distinct hypolimnetic oxygen depletion in Iron Gate reservoir. Oxygen depletion was not as intense and did not reach as high in the water column in Iron Gate reservoir as in Copco reservoir, a reflection of the relatively greater volume of water below 20 m depth in Iron Gate reservoir compared to Copco. Iron Gate reservoir also had a distinct dissolved oxygen minimum at approximately 10 to 12 m, absent from Copco reservoir, in June and July.

Photosynthetic activity pushed the pH to above 8.0 in the upper 5 m of Iron Gate reservoir from May through September, with values exceeding 9.2 in July and August. Values in other months and deeper in the reservoir range between approximately 7.0 to 7.6 units.

Specific conductance in Iron Gate reservoir followed a pattern similar to Copco reservoir, but with a reduced range of values over the year. Values in the hypolimnion stayed relatively high throughout the period of stratification while values in the epilimnion fluctuated from month to month with high values in May and June and lower values through most of the rest of the year. This pattern is similar to that of the influent water (above Copco reservoir) as shown in Figure 6. The relatively constant higher values observed in the hypolimnion are the result of the higher conductivity water from early in the year becoming isolated from exchange with the epilimnion during the period of thermal stratification.

Nutrients

Nutrient data collected from Iron Gate reservoir in 2009 are presented in Figure 25. Summary statistics are provided in Table 8. Although the seasonal temperature regime of Copco and Iron Gate reservoirs was similar, the seasonal pattern of nutrient concentrations differed. Inorganic nitrogen at the surface was high in January but low from May through September before increasing to near January values in October through November. At 40 m depth NO₃ decreased steadily through the summer while NH₃ increased steadily. Total inorganic nitrogen remained constant from May through September suggesting that conversion from NO₃ to NH₃ was facilitated in the low-oxygen environment of the hypolimnion.

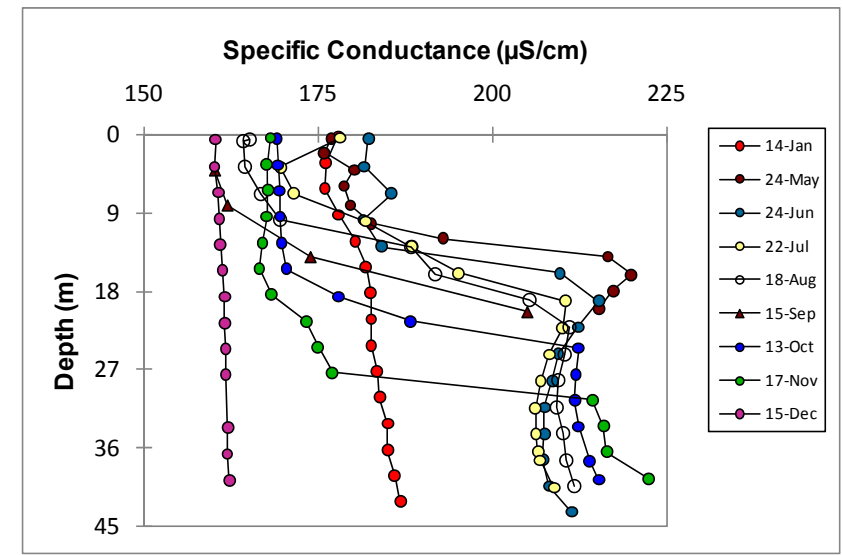
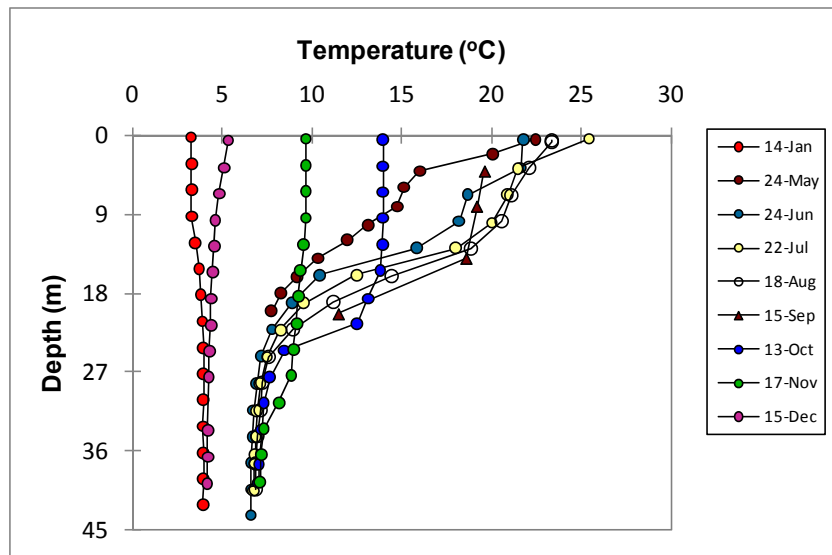
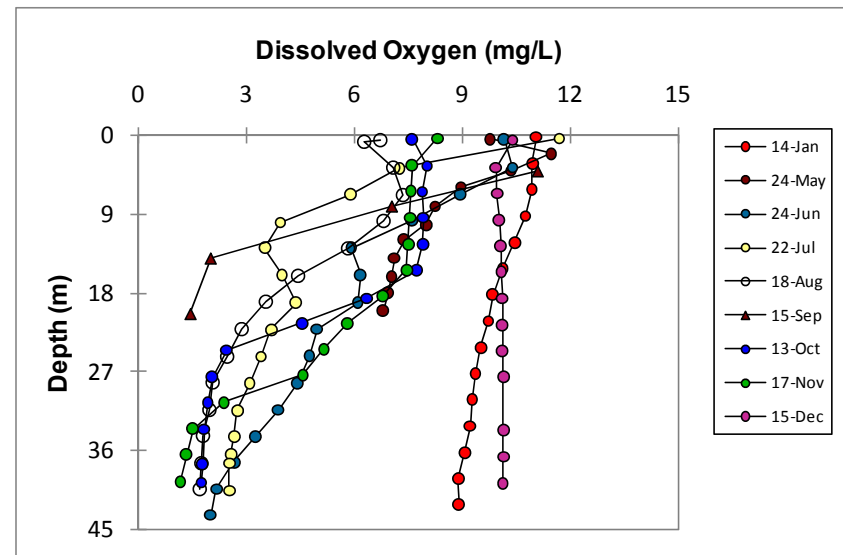
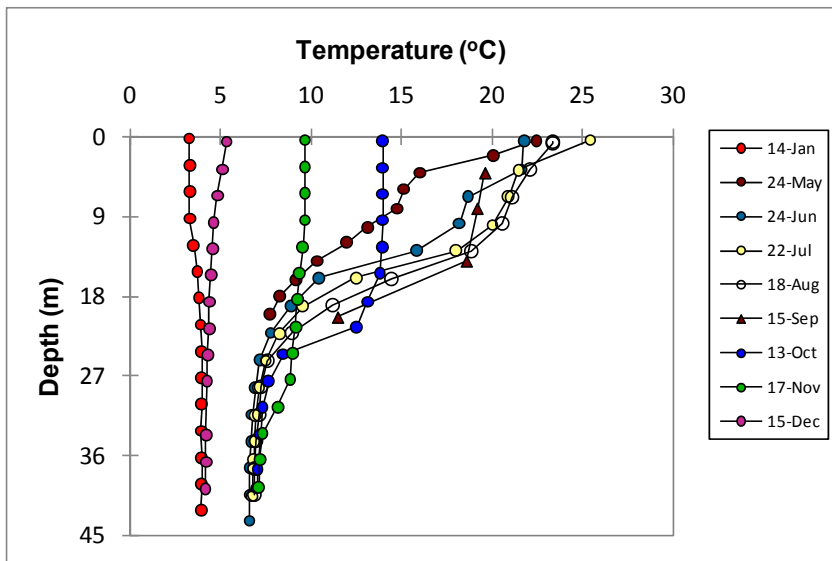


Figure 24. The results of vertical profile measurements for temperature, dissolved oxygen, pH, and specific conductance in Iron Gate reservoir in 2009.

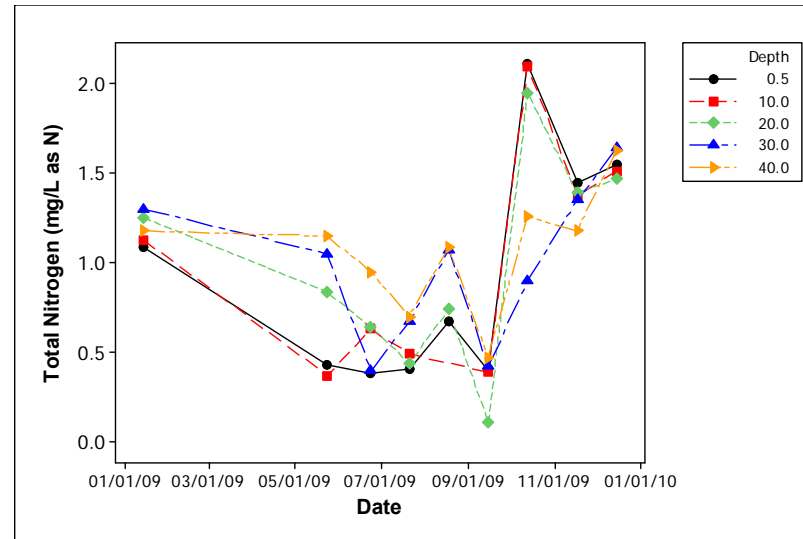
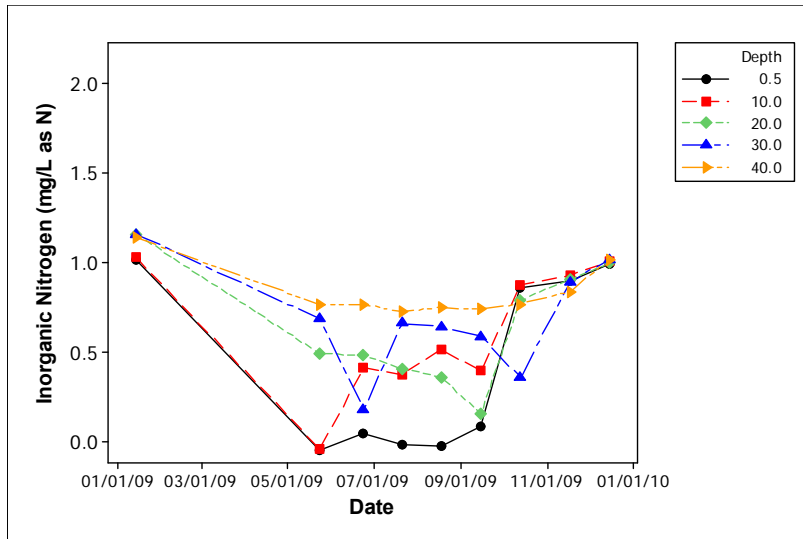
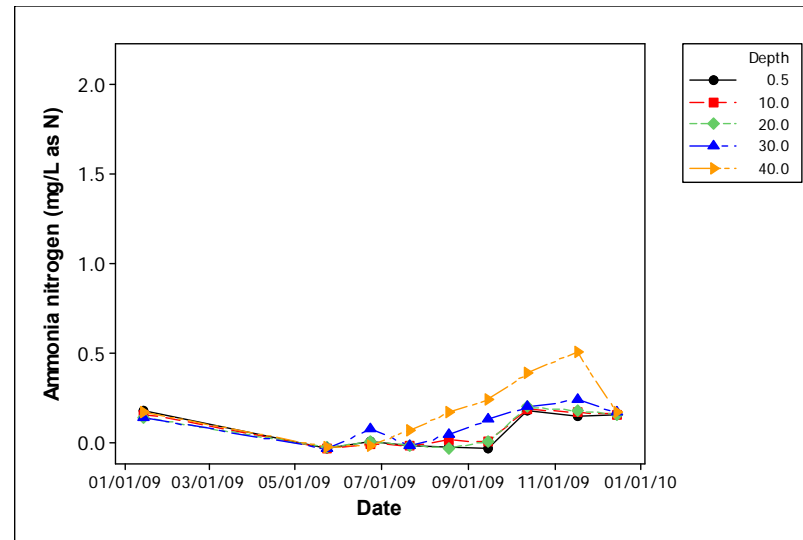
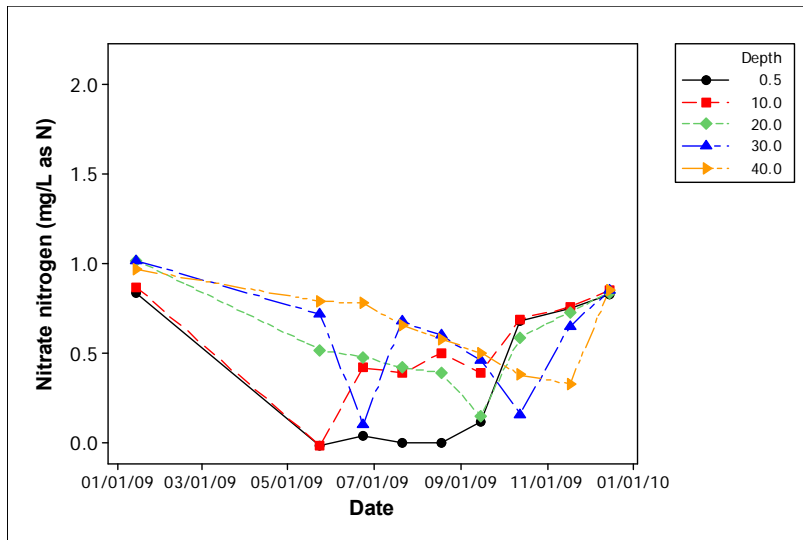


Figure 25. The results of analysis for forms of nitrogen and phosphorus in water samples collected at various depths in Iron Gate reservoir in 2009.

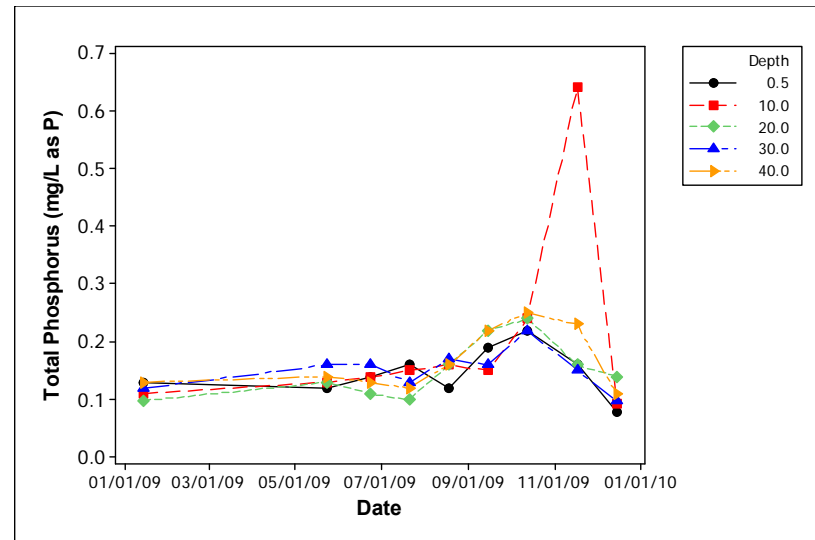
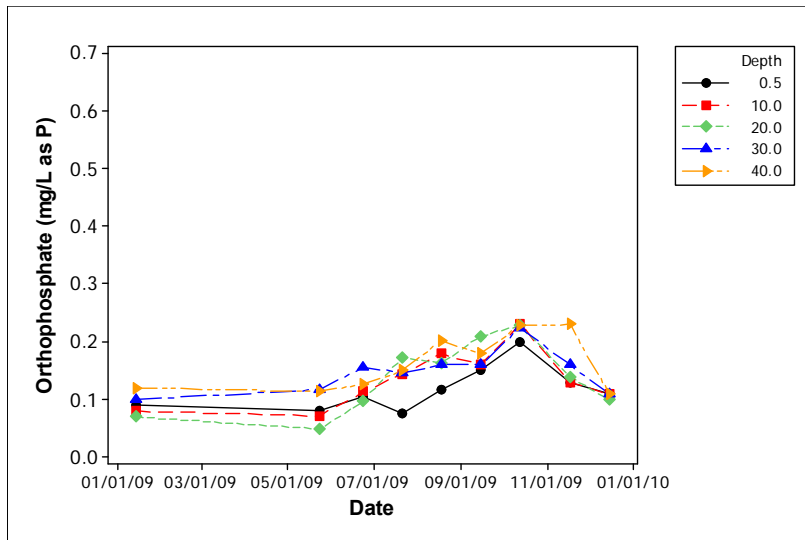


Figure 25. Continued.

Table 8. Summary statistics for nutrient samples analyzed from Iron Gate reservoir in 2009.

Descriptive Statistics for Depth = 0.5 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.064	0.361	0.943	0.424	0.118	0.147
SD	0.100	0.398	0.637	0.495	0.039	0.042
Minimum	0.00	0.00	0.38	0.00	0.08	0.079
Median	0.008	0.12	0.67	0.086	0.11	0.14
Maximum	0.18	0.84	2.11	1.02	0.2	0.22
MAD	0.0418	0.132	0.29	0.131	0.02	0.02
Descriptive Statistics for Depth = 10 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	8	9	9	9
Mean	0.072	0.540	1.000	0.612	0.134	0.202
SD	0.094	0.283	0.632	0.368	0.050	0.169
Minimum	0.00	0.00	0.37	0.00	0.07	0.094
Median	0.015	0.5	0.88	0.515	0.13	0.15
Maximum	0.19	0.87	2.1	1.03	0.23	0.64
MAD	0.044	0.19	0.495	0.365	0.03	0.02
Descriptive Statistics for Depth = 20 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.069	0.571	0.981	0.641	0.137	0.151
SD	0.098	0.261	0.577	0.336	0.062	0.051
Minimum	0.00	0.15	0.11	0.1574	0.05	0.098
Median	0.007	0.52	0.84	0.494	0.14	0.14
Maximum	0.2	1.02	1.95	1.16	0.23	0.24
MAD	0.0364	0.13	0.41	0.296	0.04	0.03
Descriptive Statistics for Depth = 30 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.106	0.582	0.978	0.688	0.150	0.152
SD	0.095	0.301	0.424	0.306	0.038	0.035
Minimum	0.00	0.1	0.4	0.181	0.1	0.098
Median	0.13	0.65	1.05	0.662	0.16	0.16
Maximum	0.24	1.02	1.64	1.16	0.23	0.22
MAD	0.07	0.19	0.3	0.228	0.01	0.01
Descriptive Statistics for Depth = 40 m						
	NH3	NO3	NT	TIN	PO4	PT
N	9	9	9	9	9	9
Mean	0.187	0.649	1.068	0.836	0.162	0.166
SD	0.176	0.218	0.334	0.145	0.049	0.053
Minimum	0.00	0.33	0.47	0.727	0.11	0.11
Median	0.17	0.66	1.15	0.768	0.15	0.14
Maximum	0.51	0.97	1.63	1.14	0.23	0.25
MAD	0.103	0.16	0.11	0.028	0.04	0.02

Orthophosphate and total phosphorus increased slightly at all depths from January through October, then decreased in October and November to values similar to January.

Particulates

Measures of particulates (Figure 26) demonstrate the effect of dense algal blooms in near the surface similar to the effect seen in Copco reservoir.

COMPARISON WITH EARLIER YEARS

Graphs depicting the mean and 95 percent confidence interval of the mean for selected data collected in the vicinity of the Klamath Hydroelectric project are presented at the end of this section. Two sets of comparisons are made; between upstream (above J. C. Boyle reservoir, site KR22822) and downstream (below Iron Gate dam, site KR18973), and between near-surface conditions (0.5 m) in Copco reservoir (KR19874) and near-surface conditions in Iron Gate reservoir (KR19019).

Changes in the concentration of nitrogen and phosphorus through time, and upstream and downstream of the Klamath Hydroelectric project are shown in Figure 27. The patterns for total phosphorus and orthophosphate are similar. For all samples collected since 2002 mean total phosphorus concentration below Iron Gate dam is significantly lower than above J. C. Boyle reservoir ($P < 0.001$, paired t-test). When plotted by individual years (Figure 27), it can be seen that average total phosphorus concentration below Iron Gate dam is consistently lower than it is above J. C. Boyle reservoir. Similar conditions apply for orthophosphate. In addition, it appears that average phosphorus concentration varies among years. Average phosphorus concentration during 2003 through 2005 appears to be lower than in the years prior to or after that period.

Nitrogen is also lower below Iron Gate dam than above J. C. Boyle reservoir. The difference for nitrate+nitrite nitrogen (NO_3) is significant ($P < 0.001$, paired t-test) when all values are considered. When plotted by individual years (Figure 27) it is clear that NO_3 is consistently, and frequently, significantly lower at the downstream location. There is no clear trend in NO_3 values with time, however, average NO_3 values since 2005 may possibly be higher than in earlier years. Similar conditions prevail for ammonia nitrogen (NH_3).

As might be expected the low velocity conditions that prevail in the Project reservoirs allow suspended matter to settle, and suspended solids in the Klamath River below Iron Gate dam are consistently and substantially lower than in the Klamath River above J. C. Boyle reservoir. The difference for all data is statistically significant ($P < 0.001$, paired t-test) as it is occasionally for individual years (Figure 28).

Average chlorophyll *a* concentration at both the upstream location and below Iron Gate dam has remained relatively constant from 2000 through 2009. There is little difference in the chlorophyll *a* concentration between the upstream and downstream locations – the difference in the means is not statistically significant ($P > 0.7$, paired t-test), and though the yearly average chlorophyll *a* concentration below Iron Gate dam is frequently less than above J. C. Boyle reservoir, the differences are small.

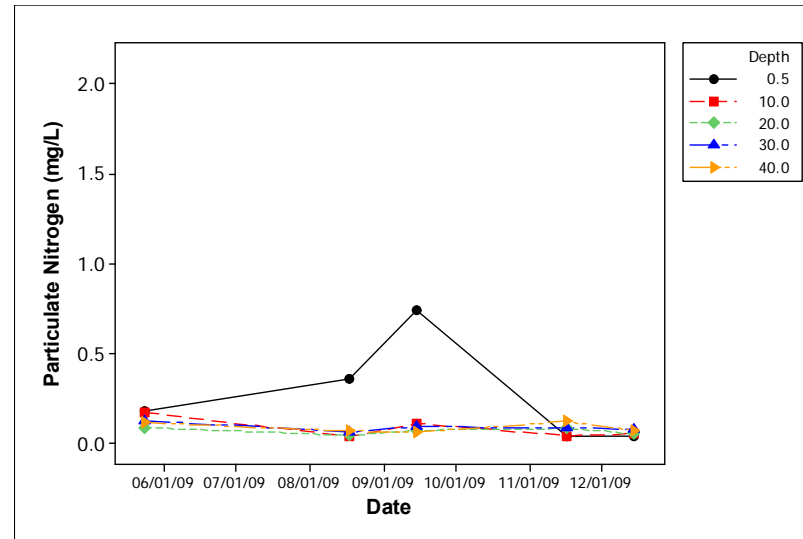
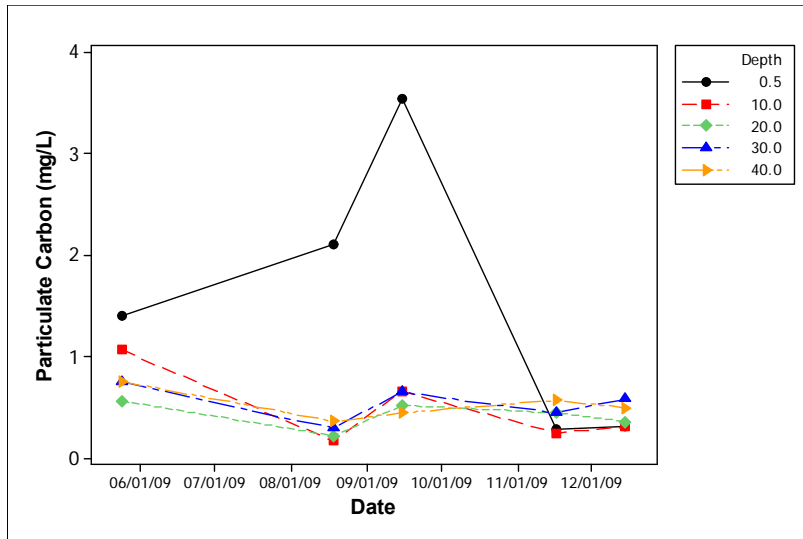
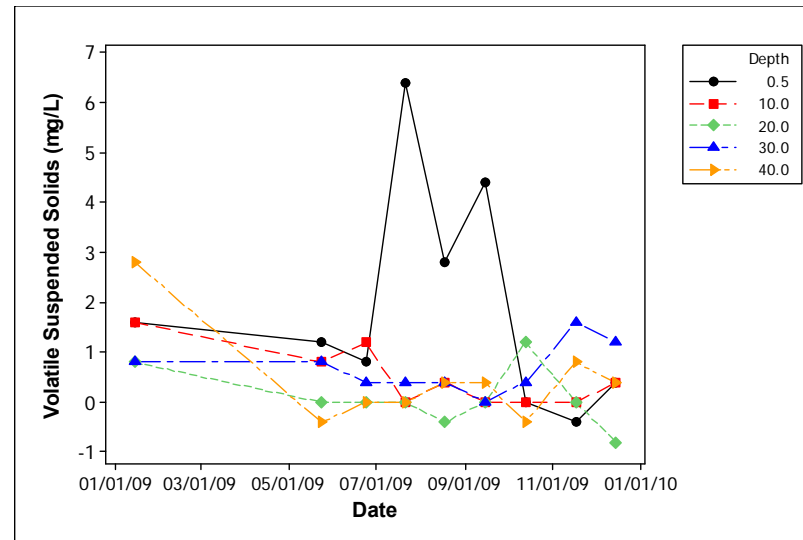
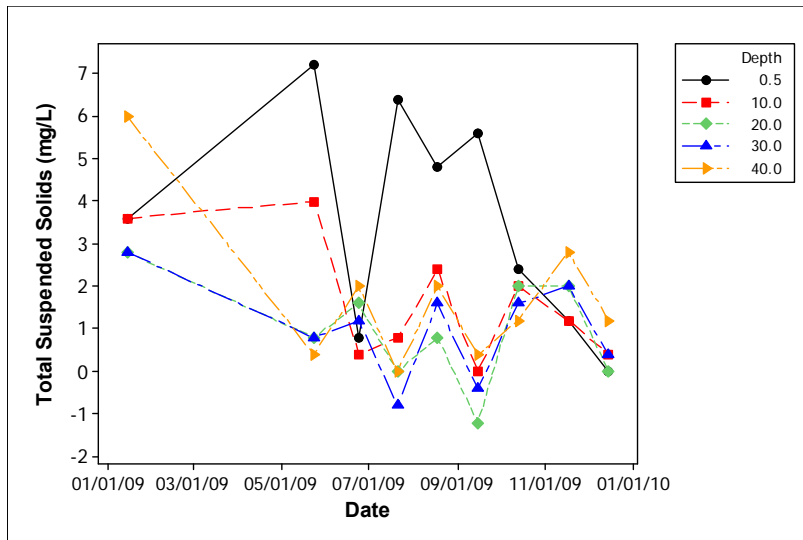


Figure 26. The results of analysis for forms of particulate matter in samples collected at various depths in Iron Gate reservoir in 2009.

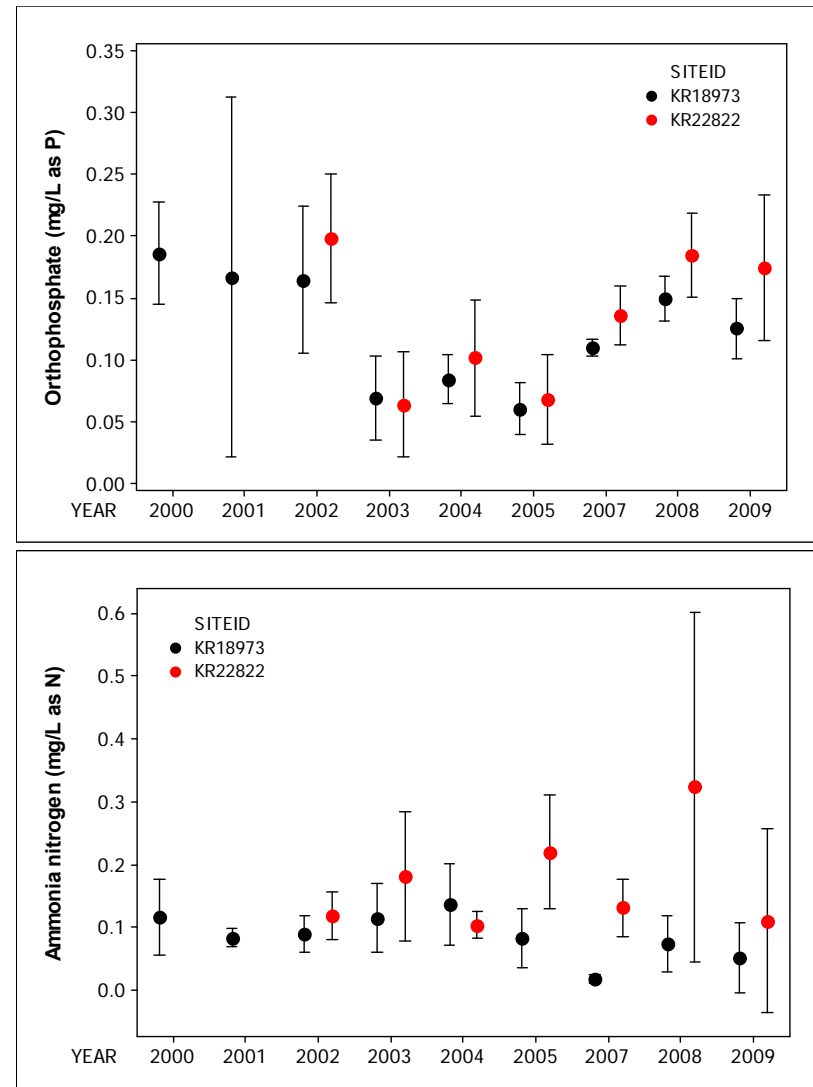
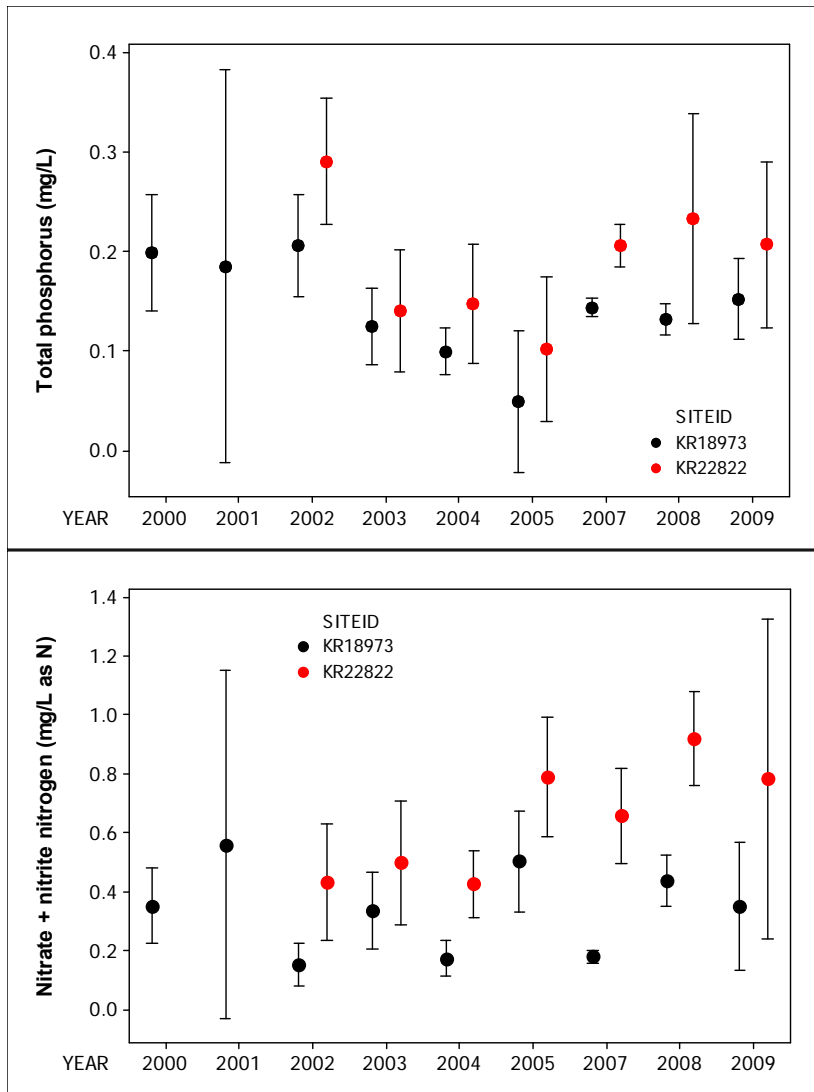


Figure 27. Mean and 95 percent confidence interval of the mean for forms of phosphorus and nitrogen measured in the Klamath River above J. C. Boyle reservoir (KR22822) and below Iron Gate dam (KR18973) from 2000 through 2009.

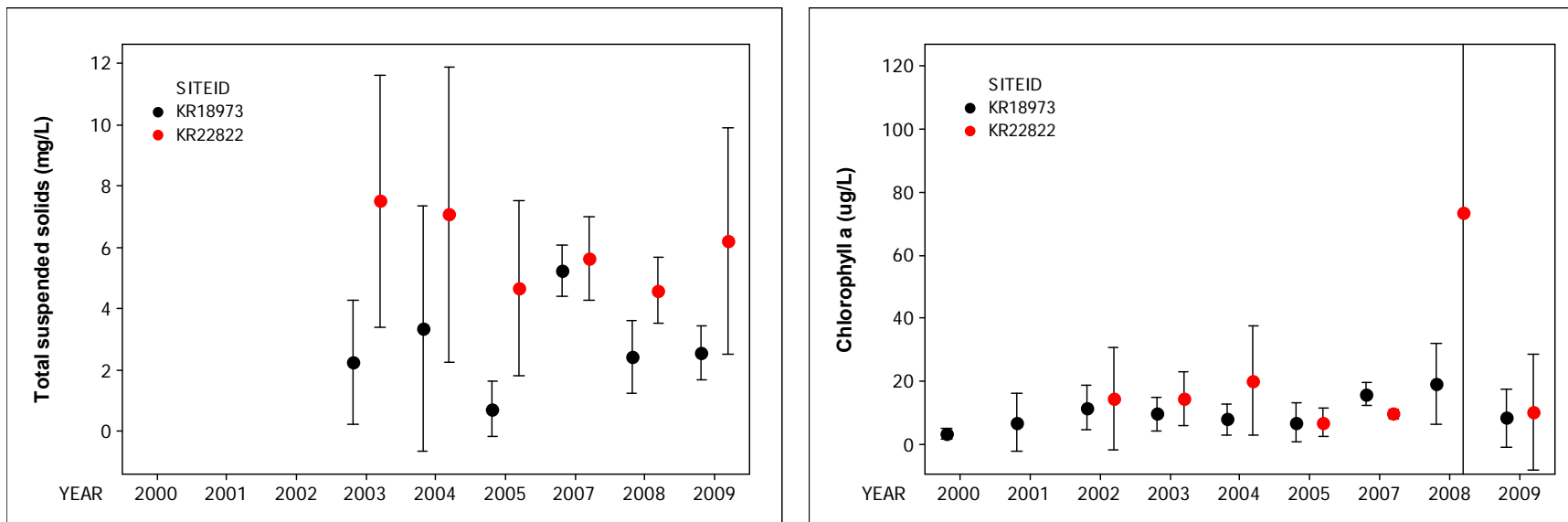


Figure 28. Mean and 95 percent confidence interval of the mean for suspended solids and chlorophyll *a* measured in the Klamath River above J. C. Boyle reservoir (KR22822) and below Iron Gate dam (KR18973) from 2000 through 2009.

Comparison of annual average values for nutrients between near-surface samples of Copco and Iron Gate reservoirs revealed that there is no significant difference between the reservoirs, although NO₃ and NH₃ tend to be lower in the surface water of Copco Reservoir than in Iron Gate reservoir (Figure 29). Total suspended solids and chlorophyll *a* values in Copco reservoir are much more highly variable than in Iron Gate reservoir.

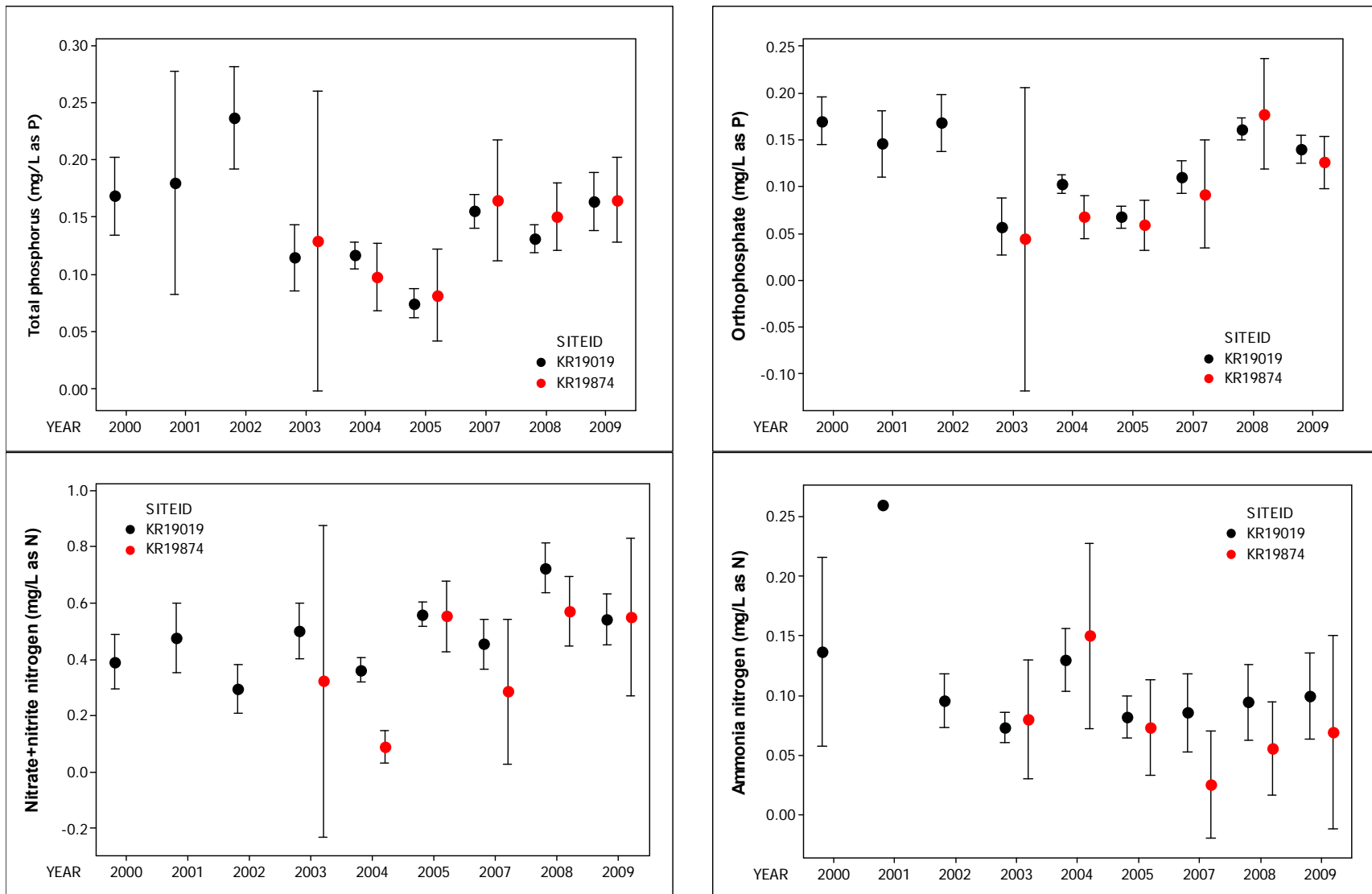


Figure 29. Mean and 95 percent confidence interval of the mean for forms of phosphorus and nitrogen measured in Copco reservoir (KR19874) and Iron Gate reservoir (KR19019) from 2000 through 2009.

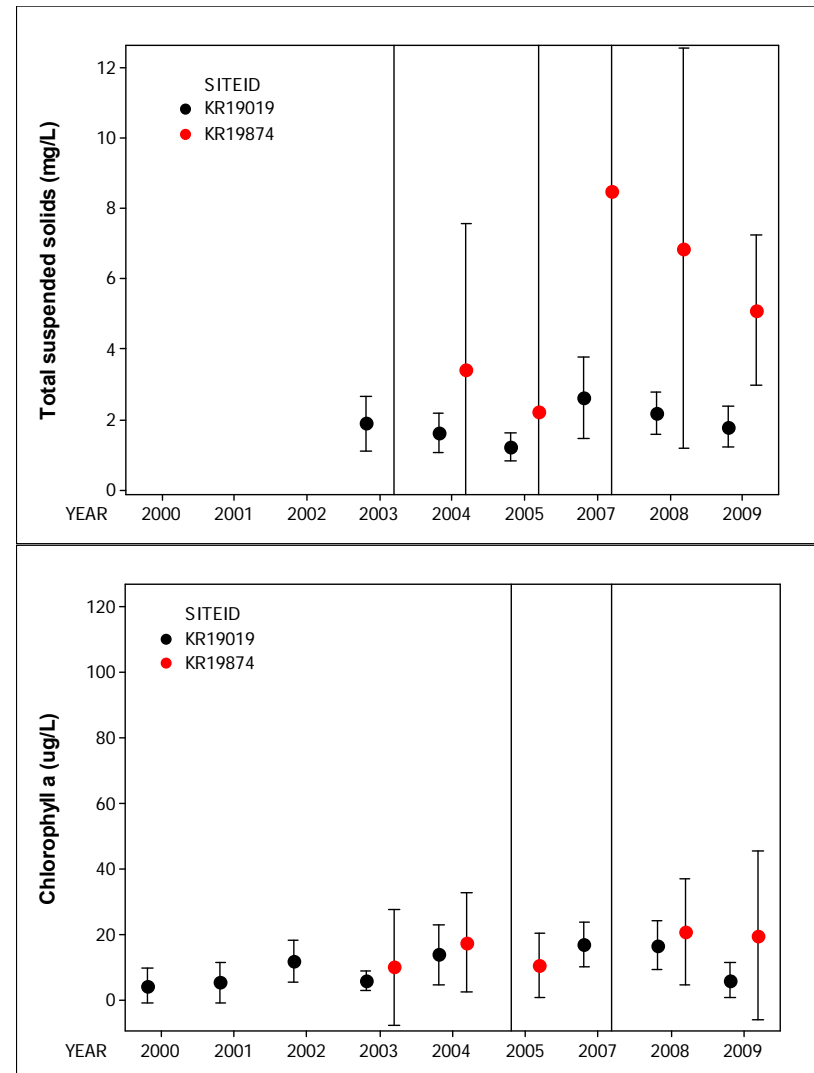
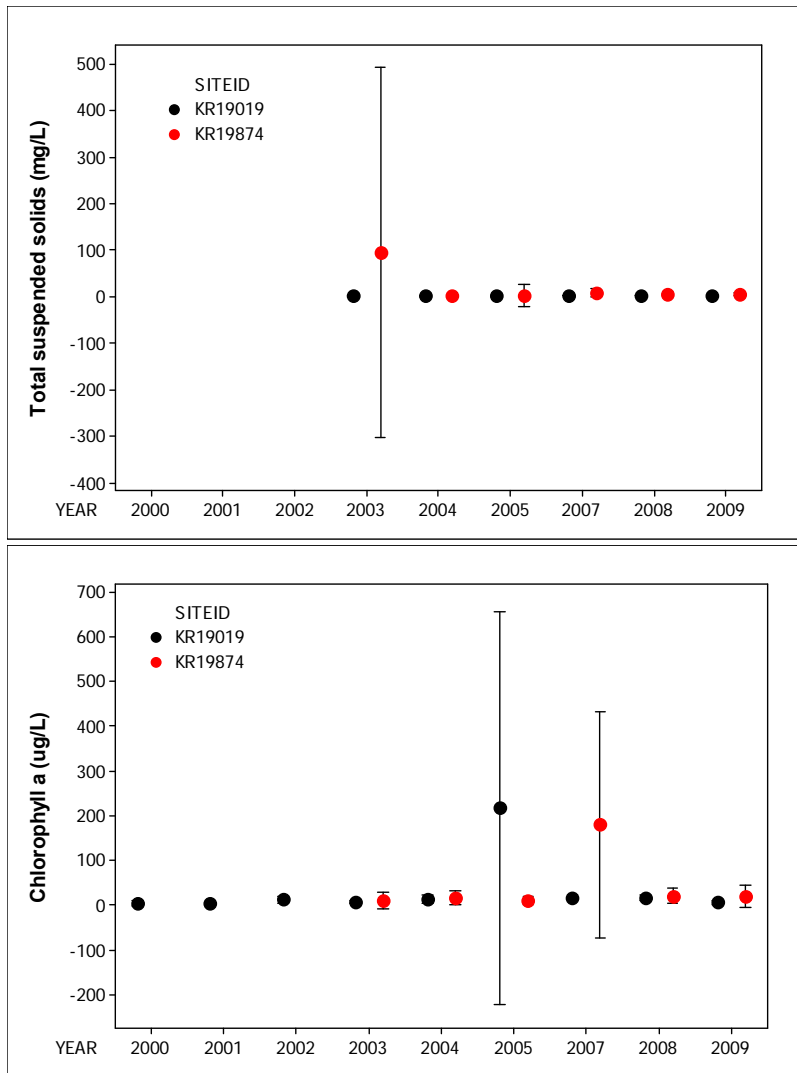


Figure 30. Mean and 95 percent confidence interval of the mean for forms of suspended solids and chlorophyll *a* measured in Copco reservoir (KR19874) and Iron Gate reservoir (KR19019) from 2000 through 2009. The scale has been expanded in the panels on the right to better view smaller values.

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**APPENDIX:
2009 QUALITY ASSURANCE REPORT**



Technical Memorandum

Date: 3/25/2009

To: Richard Raymond

From: Jennifer Vaughn, Watercourse Engineering, Inc.
Mike Deas, Watercourse Engineering, Inc.

Re: Klamath River 2009 Final External Quality Assurance Review

Summary

Of the 534 external quality assurance (QA) samples that were analyzed between May 14 and December 16, 2009 for the Klamath River 2009 water quality sampling, 72 (13.5 percent) did not meet the acceptable QA criteria used in 2009. Of those 72 samples there were one ammonium samples, two nitrate+nitrite samples, three total nitrogen samples, one total phosphorus sample, eleven orthophosphate samples, one carbonaceous biological oxygen demand samples, one microcystin sample, seventeen particulate carbon samples, nineteen particulate nitrogen samples, five chlorophyll-a samples, six chlorophyll-a Welschmeyer samples and five pheophyton samples.

In the 2009 Klamath River data set there were reported irregularities within the case narrative of two lab reports from CH2MHill, which indicated that the total nitrogen results were less than the partial nitrogen forms for four sample sets. These irregularities, combine with the total nitrogen samples which did not meet the acceptable QA criteria highlighted an issue with the method of analysis used by CH2MHill for total nitrogen on these samples. Further investigation found that 21 of the 131 nitrogen sample sets collected between May 14 and October 26, 2009 for the Klamath River water quality sampling had higher ammonium or nitrate+nitrite concentrations than total nitrogen concentrations. Phosphorus was also checked, and 34 of the 128 phosphorus sample sets had higher phosphate concentrations than total phosphorus concentrations.

Introduction

The PacifiCorp Klamath River 2009 (KR2009) water quality sampling included external quality assurance (QA) samples. The samples were collected from May 14, 2009 through December 16, 2009. Field work was performed by E&S Environmental (E&S) and laboratory analysis was performed by CH2MHill Applied Sciences Laboratory (CH2MHill), except for those constituents listed below.

- Orthophosphate analysis was performed by E&S, using a Hach Model DR2400 field spectrophotometer, with a method equivalent to the EPA 365.2 method.
- Particulate carbon, particulate nitrogen, chlorophyll-a, chlorophyll-a Welchmeyer, and pheophytin analysis was performed by Chesapeake Bay Laboratory (CBL).

- Microcystin analysis was performed by EPA Region 9 Laboratory (EPA).

Laboratory oversight and post-laboratory quality assurance was performed by Watercourse Engineering, Inc. (Watercourse). The sampling dates for the data received from the laboratory are presented in Table 1.

There were 2,490 valid samples of water collected for analysis from 17 sites. Of those samples, 534 were external QA samples from two sites. Sampling sites are presented in Table 2. Water samples were analyzed for ammonium (NH₄), nitrate+nitrite (NO₃+NO₂), total nitrogen (NT), orthophosphate (PO₄), total phosphorus (PT), total suspended solids (TSS), volatile suspended solids (VSS), alkalinity (ALKT), dissolved organic carbon (DOC), carbonaceous biological oxygen demand (CBOD), microcystin (MCYN), chlorophyll-a (CHLA), chlorophyll-a Welschmeyer (CHLA-W), and pheophytin (PHEO). Also, some samples were analyzed for total nitrogen using an unpreserved water sample (NT Unpreserved) and total Kjeldahl nitrogen (TKN) using a preserved water sample, as part of an effort to understand an underlying issue with the total nitrogen results. The project incorporated external QA samples as per the Quality Assurance Project Plan (QAPP) adopted by Watercourse, E&S, and PacifiCorp: ten percent of samples are spikes, ten percent of samples are duplicates and five percent of samples are blanks, per sampling session, throughout the sampling period.

Table 1. Sampling dates for KR2009.

Collection Dates							
May	June	July	August	September	October	November	December
5/14/2009	6/8/2009	7/6/2009	8/3/2009	9/8/2009	10/12/2009	11/16/2009	12/14/2009
5/24/2009	6/23/2009	7/20/2009	8/17/2009	9/14/2009	10/13/2009	11/17/2009	12/15/2009
5/25/2009	6/24/2009	7/21/2009	8/18/2009	9/15/2009	10/14/2009	11/18/2009	12/16/2009
5/23/2009		7/22/2009	8/19/2009	9/16/2009			
				9/21/2009			
				9/28/2009			

Table 2. External QA sampling sites of KR2009 (bold indicates external QA site).

Site ID	Site Name	Sample Depth, m	Approximate River Mile
KR18973	Klamath River below Iron Gate Dam at Hatchery bridge	0.5	189.73
KR19019	Iron Gate Reservoir	0.5	191.19
KR19019	Iron Gate Reservoir	10	191.19
KR19019	Iron Gate Reservoir	20	191.19
KR19019	Iron Gate Reservoir	30	191.19
KR19019	Iron Gate Reservoir	40	191.19
KR19645	Klamath River below Copco 2 powerhouse	0.5	196.45
KR19874	Copco Reservoir	0.5	198.74
KR19874	Copco Reservoir	9	198.74
KR19874	Copco Reservoir	18	198.74
KR19874	Copco Reservoir	27	198.74
KR20642	Klamath River above Shovel Ccreek	0.5	206.42
KR22000	Klamath River below J.C. Boyle powerhouse at Spring Island	0.5	220.00
KR22460	Klamath River below J.C. Boyle Dam	0.5	224.60
KR22478	J.C. Boyle Reservoir	0.5	224.78
KR22478	J.C. Boyle Reservoir	8	224.78
KR22822	Klamath River above J.C. Boyle Reservoir	0.5	228.22

Quality Assurance Review

Laboratory results for external QA samples were acceptable for most sample parameters. QA samples exceeding the adopted acceptance criteria were submitted for reanalysis when appropriate. Reanalysis results that confirmed the original results for the QA samples indicated one of several possibilities: a manufacturer error in QA spikes, uncertainty introduced in field procedures, or uncertainty introduced in laboratory practices. The QAPP guidelines accept the original results of a QA sample as reliable when the laboratory is able to confirm the original results with reanalysis. If the laboratory is unable to confirm the original results for a QA sample, QA guidelines assert the need to submit the entire sample batch of production and QA samples for reanalysis. However, the CH2MHill laboratory was unable to perform reanalysis in a timely manner during 2009 and the long processing time generally precluded reanalyzing entire sampling batches within acceptable sample hold times. As such, entire batch reanalysis was not performed for this project. Samples analyzed by E&S, CBL, and EPA could not be reanalyzed. Likewise, CBOD and orthophosphate, due to the short hold time, were not reanalyzed.

Quality Assurance Criteria

There were several criteria or QA assessment values used for determining the acceptability of sample results. Blank sample concentration criteria required that sample concentration be less than ten percent of the lowest sample concentration reported in its batch or less than or equal to twice the reporting limit. Duplicate sample criteria depended on the sample concentration and the reporting limit. For concentrations greater than or equal to five times the reporting limit, the Relative Percent Difference (RPD) should be less than 20% (Equation 1) or for concentrations less than five times the reporting limit, values of the duplicate sample and regular sample should vary by (plus or minus) the reporting limit. Finally, the spike sample criteria depended on the

sample concentration and the known spike concentration. For sample concentrations that are less than five times the spike concentration, the recovery should fall between 80 and 120% (Equations 2 and 3) or for sample concentrations that exceed five times the spike concentration, the difference between the spike sample and the spike concentrations must be less than the reporting limit. Due to lab and data QA processing times, most samples were reanalyzed at or just beyond the identified hold times. Further detail of the QA criteria can be found in the 2009 USBR QA protocol document “Standard Operating Procedures for Quality Assurance. Revision 2009-05.”

$$RPD = \frac{[Regular] - [Duplicate]}{[M]} \times 100 \quad (1)$$

$$\text{Recovery for Added Spike} = \frac{[Spike] - [M]}{[Spike Material Added]} \times 100 \quad (2)$$

$$\text{Recovery for Reference Solution} = \frac{[Spike]}{[Reference Solution]} \times 100 \quad (3)$$

where: M = Mean of Regular and Duplicate Concentrations

Regular = Concentration of regular sample

Duplicate = Concentration of duplicate sample

Spike = Concentration of either spiked sample or reference solution

The criteria presented above are often used as guidelines in quality assurance processes and QA assessment values that are close to the criteria limits may be identified as acceptable. The extent to which the acceptable limits are expanded is dependent upon several factors, including the laboratory performance of the specified constituent’s QA assessment during the course of the current or previous studies, the type of QA sample involved, and the adherence to the standard operating procedure (SOP) during the sample collection. During KR2009, the criteria were relaxed for samples relatively close to meeting QA requirements (these are considered approximately acceptable). The RPD value was acceptable up to 22.1 percent and the spike/reference solution recovery limits were accepted down to 76.7 percent. During the QA review of KR2009 all approximately acceptable QA assessment values are included as acceptable.

The completeness was calculated per project and also per constituent (Equation 4). The total average completeness for KR2009 was 90 percent, excluding the NT Unpreserved and TKN samples collected to investigate the NT method issue. Individual completeness percentages are presented in Table 3.

$$\text{Completeness} = \frac{\text{samples that were actually collected and analyzed}}{\text{samples that were planned to be collected and analyzed}} \quad (4)$$

Table 3. Individual constituent completeness percentages.

Constituent	Planned Samples	Analyzed Samples	Completeness	TOTAL PROGRAM AVERAGE COMPLETENESS
NH4	185	175	95%	90%
NO3+NO2	185	175	95%	
NT	185	175	94%	
PT	185	175	95%	
PO4	185	175	92%	
TSS	185	175	95%	
VSS	185	175	96%	
ALKT	185	175	85%	
DOC	185	175	97%	
CBOD	185	175	81%	
MCYN	185	175	77%	
PC	185	175	82%	
PN	185	175	82%	
CHLA	185	175	89%	
CHLA-W	185	175	89%	
PHEO	185	175	89%	
<i>NT-unpreserved</i>	<i>185</i>	<i>175</i>	<i>95%</i>	
<i>TKN</i>	<i>185</i>	<i>175</i>	<i>95%</i>	

KR2009 QA Assessment Summary

During the KR2009, 534 QA samples were analyzed.

Quality Assurance Sample Type Summary

Blanks

A total of 225 blank samples were analyzed. 31 of those blanks did not meet the acceptable QA criteria. None of the blanks were reanalyzed.

Regulars / Duplicates

A total of 228 regular duplicate sample pairs were analyzed. 36 regular duplicate pairs did not meet the acceptable QA criteria. Of those 36 pairs, three were reanalyzed and two original results were confirmed.

Spikes

There were 81 spike samples were analyzed. Of those samples, five did not meet the acceptable QA criteria. Four of the five samples were reanalyzed and three of the original results were confirmed.

Laboratory QC Reports

There were a total of twelve laboratory reports from CH2MHill, which contained their QC information. There were no lab reports with QC information from CBL, E&S Environmental, or EPA.

Of the twelve laboratory reports from CH2MHill, ten reported that all calibration, method blank, and lab control sample acceptance criteria were met, as well as the duplicate and spike sample analysis being performed in accordance with standard operating procedure. One laboratory report (i2304) noted that the method blank result for BOD of 2.3 mg/l was over the reporting limit of 2.0 mg/l, but that the samples were not set outside of holding time. All other laboratory QC results for that report were considered acceptable and were performed in accordance with standard operating procedure. Another report (i2986) noted that the duplicate RPD for KR9299 for TSS of -15.9 percent did not meet their acceptable criteria for TSS analysis of RPD < 10 percent. Also noted in that report was that the matrix spike and matrix spike duplicate recovery of total nitrogen (132 percent and 159 percent respectively) for sample KR9274 did not meet their acceptable criteria of 85-115 percent. The matrix spike duplicate RPD (8.94 percent) did meet their acceptance criteria of RPD < 15 percent. The calibration, method blanks and lab control samples were all within acceptable criteria for this report.

Constituent Summary

Ammonium

There were 42 ammonium QA samples analyzed. One of those samples did not meet the acceptable QA criteria. The single ammonium sample was reanalyzed and the original results were not confirmed.

Nitrate+nitrite

There were 42 nitrate+nitrite samples QA analyzed. Two of those samples did not meet the acceptable QA criteria. Both of those samples were reanalyzed and both of the original results were confirmed.

Total Nitrogen

There were 42 total nitrogen samples QA analyzed. Three of those samples did not meet the acceptable QA criteria. Those samples were reanalyzed and two of the original results were confirmed.

OrthoPhosphate

There were 39 ortho-phosphate QA samples analyzed. Eleven of those samples did not meet the acceptable QA criteria. However, E&S Environmental procedure did not allow for reanalysis, so none of the eleven samples were reanalyzed.

Total Phosphorus

There were 42 total phosphorus QA samples analyzed. One of those samples did not meet the acceptable QA criteria. That sample was reanalyzed and the original result was confirmed.

Total Suspended Solids

There were 42 total suspended solids QA samples analyzed. All of those samples met the acceptable QA criteria.

Volatile Suspended Solids

There were 32 volatile suspended solids QA samples analyzed. All of those samples met the acceptable QA criteria. Volatile suspended solids QA samples did not include spike samples.

Alkalinity

There were 40 alkalinity samples analyzed. All of those samples met the acceptable QA criteria.

Dissolved Organic Carbon

There were 41 dissolved organic carbon QA samples analyzed. All of those samples have met the acceptable QA criteria.

Carbonaceous Biological Oxygen Demand

There were eighteen carbonaceous biological oxygen demand QA samples analyzed. Three of those samples did not meet the acceptable QA criteria. The short hold time of 48 hours for carbonaceous biological oxygen demand analysis does not allow for reanalysis of this constituent.

Microcystin

There were fourteen microcystin QA samples analyzed. One of those samples did not meet the acceptable QA criteria. EPA procedure did not allow for reanalysis of microcystin samples. Microcystin QA samples did not include spike samples.

Particulate Carbon

There were 28 particulate carbon QA samples analyzed. Seventeen of those samples did not meet the acceptable QA criteria. CBL procedure did not allow for reanalysis of particulate carbon samples. Particulate carbon QA samples did not include spike samples.

Particulate Nitrogen

There were 28 particulate nitrogen QA samples analyzed. Nineteen of those samples did not meet the acceptable QA criteria. CBL procedure did not allow for reanalysis of particulate nitrogen samples. Particulate nitrogen QA samples did not include spike samples.

Chlorophyll-a

There were 26 chlorophyll-a QA samples analyzed. Five of those did not meet the acceptable QA criteria. CBL procedure did not allow for reanalysis of chlorophyll-a samples. Chlorophyll-a QA samples did not include spike samples.

Chlorophyll-a Welchmeyer

There were 26 chlorophyll-a Welchmeyer QA samples analyzed. Six of those did not meet the acceptable QA criteria. CBL procedure did not allow for reanalysis of chlorophyll-a Welchmeyer samples. Chlorophyll-a Welchmeyer QA samples did not include spike samples.

Pheophytin

There were 26 pheophytin QA samples analyzed. Five of those did not meet the acceptable QA criteria. CBL procedure did not allow for reanalysis of pheophytin samples. Pheophytin QA samples did not include spike samples.

Total Nitrogen on unpreserved sample

For the special investigation into the total nitrogen method used by CH2MHill, there were four NT Unpreserved QA samples analyzed. All of those samples met the acceptable QA criteria. NT-unpreserved QA samples did not include spike samples.

Total Kjeldahl Nitrogen

For the special investigation into the total nitrogen method used by CH2MHill, there were four TKN QA samples analyzed. All of those samples met the acceptable QA criteria. TKN QA samples did not include spike samples.

Total versus Partial Nutrient Summary

There were 99 instances in the KR2009 data set where there were ammonium, nitrate+nitrite and total nitrogen results for one sample and all of the results were above their respective reporting limits, and therefore a comparison of the total nitrogen and the sum of ammonium and nitrate+nitrite was possible. Of those 99 comparisons, three showed higher concentrations of the sum of ammonium and nitrate+nitrite than total nitrogen, and six had total nitrogen results within 20 percent RPD of the sum of ammonium and nitrate+nitrite, indicating similar values. Both the comparisons with similar values and the comparisons where total nitrogen values were less than the sum of ammonium and nitrate+nitrite indicate an issue, as total nitrogen in the Klamath River system should include a large portion of organic nitrogen and should be considerably larger than the sum of the inorganic nitrogen forms.

There were 157 instances in the KR2009 data set where there were both orthophosphate and total phosphorus results for one sample and all of the results were above their respective reporting limits and therefore a comparison of the total phosphorus and its partial form was possible. Of those 157 comparisons, three showed higher concentrations of the ortho-phosphate than total phosphorus, and 34 had total phosphorus results within 20 percent RPD of the ortho-phosphate values, indicating similar values. The comparisons with similar results do not represent an issue as organic phosphorus levels in the Klamath River system are relatively small. However, the comparisons where total phosphorus was less than ortho-phosphate indicate an issue, as total phosphorus should remain higher than ortho-phosphate regardless of the amount of organic phosphorus in the system.

Quality Assurance Issues of KR2009

During the QA assessment process for KR2009 some issues pertaining to the QA samples were identified. These issues are discussed below.

Delay in receipt and use of spikes and reference solutions

Spikes and reference solutions were not available with sufficient lead time due to contracting issues to allow spiked samples or reference solutions to be included in the early sample collection. Therefore, the initial sets of samples are not associated with full external QA sets.

Use of reference solution as spike solution

During three sets of samples, a reference solution was used as a spike and added to environmental water to create a spiked sample for alkalinity. An average alkalinity value of the environmental water was calculated from the regular and duplicate samples and subtracted from the spike sample value to determine the recovery of these samples.

Use of environmental water in blank sample

During four sets of samples, the results of the alkalinity blank or the CBOD blank were of the same order of magnitude as the results of the regular and duplicate samples, indicating that environmental water was used instead of distilled (or dionized) water. One of these samples was reanalyzed and the original results were confirmed. The other blank samples with these characteristics was not reanalyzed.

CBOD hold times exceeded

There were six reports in which the CH2MHill laboratory noted that the 48-hour hold time for CBOD had been exceeded prior to receipt of the samples or that the samples were received without sufficient holding time remaining for CBOD analysis to be completed. As a result, there were 21 CBOD samples that were analyzed past hold times during the course of the sampling program.

Table 4. CBOD samples which were received outside of hold time or which were received without sufficient time for analysis

Sample ID	Received outside hold time	Received without sufficient time for analysis
KR9015	X	
KR9016		X
KR9025		X
KR9033		X
KR9050	X	
KR9138	X	
KR9139	X	
KR9148	X	
KR9156	X	
KR9215		X
KR9216		X
KR9225		X
KR9233		X
KR9246	X	
KR9247	X	
KR9256	X	
KR9264	X	
KR9273	X	
KR9274		X
KR9283		X
KR9291		X

Improper method for total nitrogen analysis

A quality control concern was identified with the total nitrogen analysis method employed by the CH2MHill Applied Sciences Laboratory. Several samples in the E&S Environmental KR2009 project were reported with ammonium or nitrate+nitrite values higher than the total nitrogen³ values. The KR2009 project provided external QA spike samples for total nitrogen in which three of the four that were analyzed by October 5, 2009 had low recoveries (67.0, 62.3, and 63.0 percent). Both the low total nitrogen spike recoveries of the QA samples and the instances where either ammonium or nitrate+nitrite values were higher than the total nitrogen values suggested that the CH2MHill method may be producing results that are lower than actual values.

Review of the CH2MHill data report case narratives (where any irregularities within the data set are reported) found two lab reports for the E&S KR2009 project that mentioned total nitrogen values being less than other nitrogen form values, although this condition occurred in additional instances as well.

Upon consultation with E&S, Richard Raymond from E&S Environmental contacted CH2MHill to inform them of this issue and inquire about their method. He learned that CH2MHill has been employing a method recommended by the instrument manufacturer, which closely resembled,

³ Total Nitrogen for this project is assumed to equal the sum of ammonium, nitrate + nitrite, and organic nitrogen.

but is slightly different than Standard Methods 4500-N C Persulfate Method. Review of 4500-N C Persulfate Method indicated that the required procedures are not intended for use with preserved samples. However, a check of sample bottles delivered by the lab indicated that preservative was included (H₂SO₄). When the lab was consulted about the use of preserved sample, CH2MHill stated that the instrument manufacturer allowed for the use of preserved sample for the method being utilized.

Nonetheless, review of field data indicated that there was an issue with the measurement of total nitrogen using that method. Following the discussion with CH2MHill, TKN and total nitrogen from an unpreserved sample (NT Unpreserved) were included in the analysis of the October 13 and October 14, 2009 sample set in addition to the regular set of constituents. Regular, duplicate and blank QA samples were included for TKN and NT Unpreserved, but no spike QA sample was included for either constituent. Total nitrogen (NT) was calculated as TKN plus nitrate+nitrite. The calculated total nitrogen (Calculated NT) value was compared to the NT Preserved and NT Unpreserved samples using an RPD value, calculated from Equation 5.

$$RPD = \frac{[Calculated\ NT] - [NT\ measured]}{[M]} \quad (5)$$

where RPD = Relative Percent Difference (%)

Calculated NT = Calculated Total Nitrogen (mg/l)

NT measured = NT Preserved or NT Unpreserved (mg/l)

M = Mean of calculated and measured total nitrogen (mg/l)

RPD values at or below 20 percent are considered similar values, whereas RPD values above 20 percent are considered to be different.

There were 20 sets of Calculated NT, NT Preserved, and NT Unpreserved comparisons available from the October 13 and October 14, 2009 sample sessions. Of the 20 comparisons of Calculated NT and NT Preserved, 6 comparisons had RPD values of less than 20 percent (Table 5). Of the 20 comparisons of Calculated NT and NT Unpreserved, 17 comparisons had RPD values less than 20 percent. The three comparisons with RPD values above 20 percent were the two blanks (TKN method detection limit of 0.2 mg/l precludes reliable comparison at values at or below 0.2 mg/l) and one the sample with the lowest concentration NT Unpreserved value. This indicates that the unpreserved total nitrogen results were more similar to the calculated total nitrogen results which used TKN and nitrate+nitrite.

Table 5. Summary of calculated NT and NT Preserved and Unpreserved comparison results.

Comparison Set	Number of Sets	RPD ≤ 20 Percent	RPD > 20 Percent
Calculated NT and NT Preserved	20	6	14
Calculated NT and NT Unpreserved	20	17	3

Included in the October 13 and October 14 normal constituent data set are the two spike QA samples for NT Preserved that had recoveries of 89 percent (KR9224) and 92 percent (KR9236).

Both fall within the acceptable recovery range of 80 percent to 120 percent. This indicated that the NT Preserved spike sample results were accurate, unlike the previous NT Preserved spike samples results, which were too low.

However, there were some trends in the NT Unpreserved and NT Preserved data set that should be noted. When the values were below the reporting limit for total nitrogen (0.2 mg/l), the RPD values were extremely high, indicating the uncertainty associated with values at or below the reporting limit. When the values were above the reporting limit, but relatively low (e.g., samples KR9222 and KR9223), the differences between the total nitrogen preserved and unpreserved values were notably less. Also, when the sample values were clearly higher, as in the case of the spike QA samples, the RPD between the calculated total nitrogen and the total nitrogen preserved was less than 20 percent, indicating that the total nitrogen preserved results were similar to the calculated values. The mid-range NT Preserved values were the most dissimilar to the Calculated NT values, whereas the NT Unpreserved samples were similar to the Calculated NT values over the entire range of results, except those results at or below the reporting limit.

The new data set shows the NT Preserved samples to be consistently higher than the NT Unpreserved and the Calculated NT results. The higher preserved results are at odds with the initial data set which illuminated this issue (both low spike recoveries and values of ammonium or nitrate+nitrite higher than total nitrogen), which indicated that the preserved samples were producing lower total nitrogen results than the actual concentrations. There was insufficient data to determine if the previous total nitrogen data are too low or too high.

CH2MHill returned to the samples provided to them in November 2009 after adjusting their method using preserved samples. After reanalyzing 21 samples for total nitrogen using both the preserved and non-preserved water, the lab is more confident in their method as they move forward. Of those 21 samples, all comparisons between the preserved and non-preserved results were within 20 percent RPD or their difference was less than the reporting limit of the method (0.20 mg/l) and therefore all of the preserved and non-preserved results can be considered similar. The results and RPD calculations are presented in Table 6.

Recommendations include incorporating TKN analysis for every ten samples and calculating total nitrogen (as TKN + NO₂+NO₃) as a check against the NT Preserved analysis performance.

Table 6. CH2MHill return analysis of preserved and non-preserved total nitrogen samples and sample comparison. RPD was calculated when the average of the preserved and non-preserved samples was greater or equal than five times the reporting limit; The absolute difference was calculated when the average of the preserved and non-preserved samples was less than five times the reporting limit.

Sample ID	CH2MHill ID	Date	Type	Reported Results		Statistic Data for RPD calculation		Calculated Values		Acceptable?	
				NT Non-preserved, mg/l	NT Preserved, mg/l	NT Non-preserved, mg/l	NT Preserved, mg/l	RPD	Difference	RPD < 20%	Diff < +-RL
KR9246	I283101	11/17/2009	R	0.88	0.85	0.88	0.85		0.03		yes
KR9247	I283102	11/17/2009	Q	1.44	1.44	1.44	1.44	0		yes	
KR9250	I283103	11/17/2009	R	1.42	1.45	1.42	1.45	2.09		yes	
KR9251	I283104	11/17/2009	R	1.48	1.38	1.48	1.38	6.99		yes	
KR9252	I283105	11/17/2009	R	1.43	1.39	1.43	1.39	2.84		yes	
KR9253	I283106	11/17/2009	R	1.39	1.35	1.39	1.35	2.92		yes	
KR9254	I283107	11/17/2009	R	1.15	1.18	1.15	1.18	2.58		yes	
KR9256	I283109	11/17/2009	B	-0.085	-0.042	0.2	0.2		0		yes
KR9259	I283110	11/17/2009	R	1.56	1.55	1.56	1.55	0.64		yes	
KR9260	I283111	11/17/2009	R	1.49	1.51	1.49	1.51	1.33		yes	
KR9261	I283112	11/17/2009	R	1.48	1.49	1.48	1.49	0.67		yes	
KR9262	I283113	11/17/2009	R	1.48	1.49	1.48	1.49	0.67		yes	
KR9263	I283114	11/17/2009	R	1.47	1.52	1.47	1.52	3.34		yes	
KR9264	I283115	11/17/2009	D	1.42	1.43	1.42	1.43	0.7		yes	
KR9265	I283116	11/18/2009	Q	2	2	2	2	0		yes	
KR9266	I283117	11/18/2009	R	1.93	1.95	1.93	1.95	1.03		yes	
KR9268	I283119	11/18/2009	B	-0.12	-0.093	0.2	0.2		0		yes
KR9269	I283120	11/18/2009	R	2.02	2.03	2.02	2.03	0.49		yes	
KR9270	I283121	11/18/2009	R	2.05	2.1	2.05	2.1	2.41		yes	
KR9271	I283122	11/18/2009	R	2.11	2.12	2.11	2.12	0.47		yes	
KR9272	I283123	11/18/2009	D	1.96	2.04	1.96	2.04	4		yes	

Types: R – production sample
Q – regular sample
B – blank sample

All spike samples were removed from considerations as there was no spike material present in the non-preserved samples.

References

U.S. Bureau of Reclamation (USBR). 2009. Standard Operating Procedures for Quality Assurance. Revision 2009-05. Environmental Monitoring Branch, Mid-Pacific Region, Sacramento, CA. May.