Okanogan River Tributaries pH 303(d) Listing Verification Study

September 2016

Publication No. 16-03-036

DEPARTMENT OF ECOLOGY
State of Washington

Publication information

This report is available on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1603036.html

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search Study ID JICA0003.

The Activity Tracker Code for this study is 16-024.

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Okanogan River Tributaries
pH
303(d) Listings Verification Study

by

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Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area:

WRIAs
- 49

HUC numbers
- 17020006
- 17020007

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Abstract

During 2015-2016, the Washington State Department of Ecology (Ecology) monitored 11 tributaries to the Okanogan River for verification of pH impairment. A total of 19 reaches on the 11 tributaries are on the Washington State 303(d) list for not meeting pH criteria.

The 303(d) listings were based on pH measurements made by the Okanogan Conservation District during a 3-year Ecology grant project from 2000 to 2003. Ecology's review of the older pH data showed a bias for the pH measurements.

Ecology conducted verification monitoring during August and October 2015 and April 2016.

Eighteen of the 19 listed reaches met pH standards. In several cases, levels were above the pH criteria but were determined to be in equilibrium with the pH saturation potential.

A model of pH saturation showed that the pH of tributaries in the Okanogan River basin was often higher than the pH criteria due to high alkalinity levels in the water. The high alkalinity is the result of natural carbonate geology in the Okanogan basin.

Data collected for this study were sufficient to show that most of the Okanogan River tributaries do not have pH impairment due to anthropogenic influences.

Acknowledgements

The author of this report thank the following Department of Ecology staff for their contributions to this study:

- Eiko Urmos-Berry for field assistance and report map figures.
- Molly Gleason for EIM data upload.
- Heather Simmons, Greg Bohn, Patrick Lizon, Chad Brown, and Kristin Carmack for review of the draft final report.
- Greg Pelletier for technical assistance and peer review.
- Jean Maust and Joan LeTourneau for publication editing and formatting.

Introduction

Background

Natural freshwater generally falls within the range of 6.0 to 9.0 pH units. A numeric scale of pH is used to specify the acidity or basicity of an aqueous solution. The U.S. Environmental Protection Agency (EPA) has issued guidance and recommends a pH range of 6.5 to 9.0 in freshwater to protect aquatic life (EPA, 1976 and 1986). Most aquatic life biota are generally adapted and fully protected within this range (Robertson-Bryan, 2004).

Washington State has adopted state-wide pH criteria between 6.5 and 8.5 to protect freshwater aquatic life. Stream pH outside this range is accommodated by Washington State standards when it is naturally occurring; however, the Washington State Department of Ecology (Ecology) is required to demonstrate that the values outside the numeric criteria are due to natural causes and not to anthropogenic causes.

Eighteen tributary sites in the Okanogan River basin, located in north-central Washington, are included on the 2012 Washington State 303(d) list of the federal Clean Water Act of impaired water bodies, because they did not meet surface water quality criteria for pH (Figure 1). An additional two tributary reaches are listed on the current 303(d) list.

The 303(d) listings are primarily based on pH measurements made by the Okanogan Conservation District (CD) during a 3-year Ecology grant project (spring of 2000 to spring of 2003) to assess water quality in the Okanogan basin. A review of the collected pH measurement data shows a potential bias over the grant project period. Ecology decided to verify the pH exceedances in 2015-2016 before conducting a more intensive Total Maximum Daily Load (TMDL) study.

Streamflow was expected to be low because of a drought in Washington during 2015. Verification measurements made in August and October 2015 were considered to be ideal for monitoring critical pH conditions. Monitoring was also performed in April 2016 to see if springtime conditions showed pH exceedances.

The sampling design consisted of three periods of diel monitoring to meet the data needs for assessing pH exceedances in surface water. Ecology's Water Quality Program has minimum requirements for the listings of water bodies for pH impairment, which include 3 daily pH exceedances during the seasons of concern when the effects of eutrophication are likely, generally spring through fall.

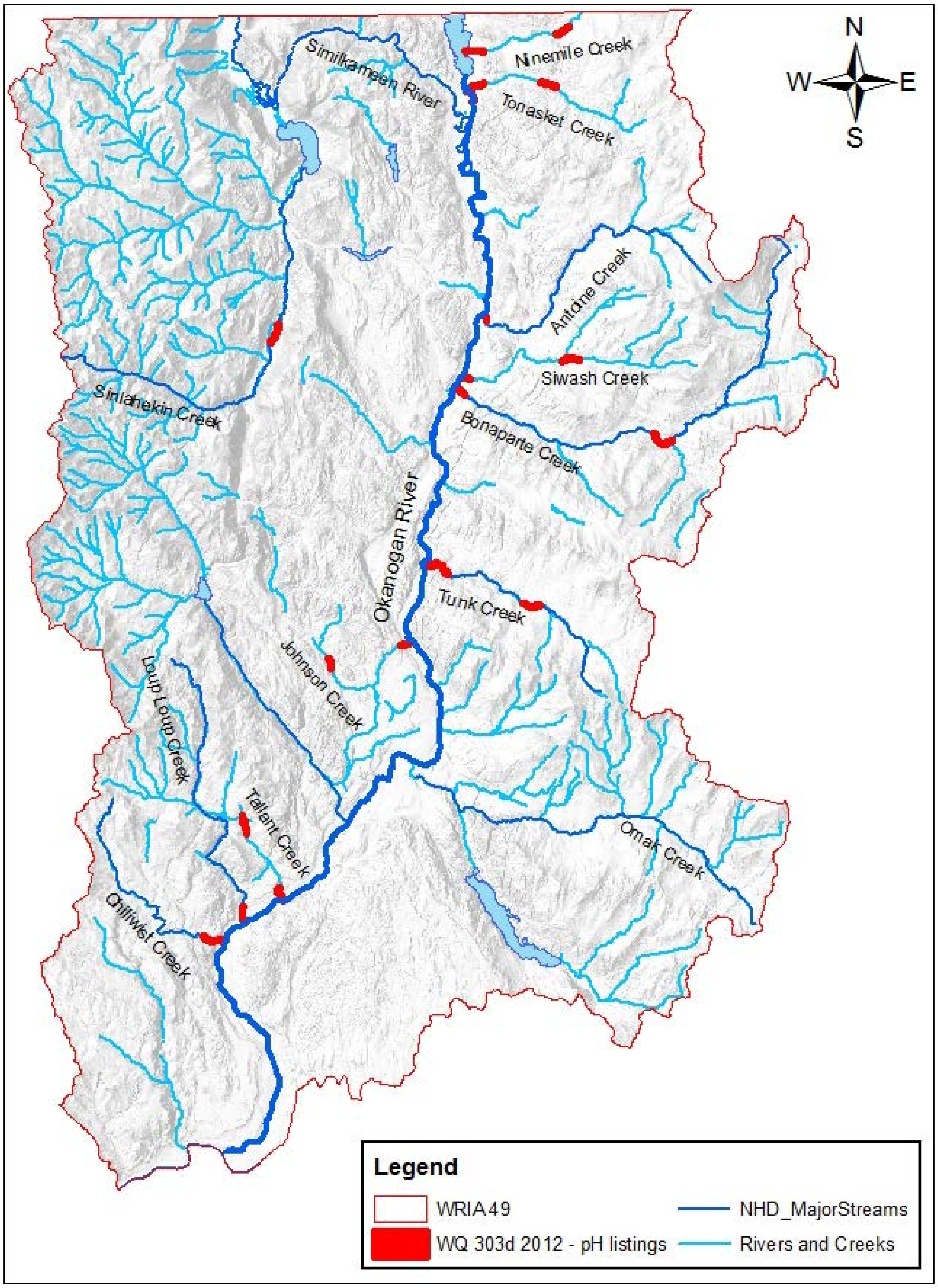


Figure 1. Study area for the *Okanogan River Tributaries pH 303(d) Listing Verification Study* showing the location of the sites with 2012 category 5 pH listings.

Separating natural from anthropogenic effects

The pH of water is a measurement of the concentration of hydrogen ions in the water. The carbonate system principally regulates the hydrogen ion concentration in freshwater. The carbonate system is composed of aqueous carbon dioxide (CO_2), carbonic acid, and carbonate ions.

The chemical make-up of water in a stream, including its carbonate system, generally reflects the geochemical make-up of the basin's rocks and soil. As precipitation passes over or through substrates, it picks up dissolved substances from the geologic material (measured as conductivity and alkalinity) which determine the pH saturation potential of the water. The pH saturation is reached when the dissolved CO_2 in the water is at equilibrium with the CO_2 in the atmosphere.

The source water to the stream may not be at saturation when it enters the stream. For instance, groundwater inflows are usually reduced (low in oxygen) and can be low in pH (oversaturated with CO_2), not in equilibrium with atmospheric gases. Many of the Okanogan River tributaries are principally groundwater-fed for most of the year.

Once the source water enters the stream, several factors control the equilibrium pH in water, which may not reach saturation. At any given location and time within an aquatic system, the observed pH reflects an equilibrium state of the pH saturation potential modulated by other physical and biological processes taking place in the water, including:

- Physical mechanics of the stream (depth, velocity, slope, and water clarity) influence biological processes and reaeration rates. Biological activity is greatest in shallow, clear periphyton-dominated streams. The reaeration rate affects if and how quickly the aqueous CO_2 in the water is able to reach an equilibrium state with the CO_2 in the overlying atmosphere.
- Biological processes, like primary productivity, affect the chemical balance of the carbonate system. The changes in dissolved inorganic carbon during photosynthesis and respiration can cause diel fluctuations in pH.
- All of the above processes are temperature-dependent, so water temperature changes affect pH as well.

Any human activities that affect the physical, chemical, or biological processes of a stream can affect the pH. The biggest impact is usually from nutrient enrichment of water which causes higher levels of biological activity leading to greater diel fluctuations in pH.

Biological processes affect pH in water through photosynthesis and respiration, which consume and produce CO_2. The diel pattern of photosynthesis during the day and respiration at night cause a diel fluctuation in dissolved inorganic carbon, and therefore in pH also. Diel pH levels typically peak in the late afternoon when inorganic carbon concentrations are lowest. Diel pH fluctuations are lowest in early morning just before photosynthesis begins. Higher biological productivity leads to a larger pH response in the water, relative to the other physical processes and buffering capacity of the water.

Geologic effect on pH in the Okanogan River basin

Accreted terranes in the Okanogan River basin introduced marine sediments to the geology of the Okanogan basin (Dawes and Dawes, 2001). Dawes and Dawes (2001) state that these terranes contain limestone and other marine (carbonate) sediments which were brought to the North American continent by plate boundary convergence sometime in the Mesozoic era.

Carbonate rocks precipitate and dissolve into carbonate and bi-carbonate ions in water, both of which are principle components in the equilibrium of freshwater ions which determine the pH of the water.

A principal carbonate mineral is calcium carbonate which contributes to a water’s alkalinity. Alkalinity is measured as the buffering capacity of a water to pH change from added acids and bases in the water. The higher the alkalinity, the higher the resistance to change in pH. Higher alkaline waters have naturally higher pH saturation levels which can even exceed the pH criteria for Washington State.

Previous monitoring

The Okanogan Conservation District (CD) received an Ecology grant (#G0000225) to conduct water quality monitoring in tributaries to the Okanogan River from the spring of 2000 to spring of 2003.

Based on the results of the monitoring, 18 out of 25 sites were listed for pH levels above the Washington State pH criteria of 6.5 to 8.5. The 18 sites are located on 11 different tributaries, with 7 tributaries having 2 segments (upper site and lower site) with pH impairment. Ecology is required to determine if the high pH levels are due to anthropogenic causes. If so, the impairments must be addressed by a TMDL study.

Prior to conducting a planned, intensive pH TMDL, Ecology reviewed the pH measurements from the Okanogan CD monitoring. Anomalies in the pH data concerned Ecology and triggered the current verification study. Figure 2 presents a time series plot of all of the pH data collected by the Okanogan CD from the spring of 2000 to the spring of 2003. Darker shaded measurements are from the 11 tributary segments (highlighted in Table 1) that Ecology re-monitored for pH.

The pH data show that the relative range of pH measurements from all sites for each monthly survey was about the same: ≈1 to 1.5 pH units. This might indicate that the measurements show the same precision for each monitoring event.

However, there appears to be a meandering bias throughout the Okanogan CD monitoring period. For example, from June of 2000 to May 2001, pH measurements were higher, with many of the sites exceeding 8.5 pH units. The pH measurements from this period of the monitoring project are the basis for most of the 303(d) pH listings. Then from June 2001 to December 2002 (the next 18 months of monitoring), almost all sites were below 8.5 pH units.

There was not a change or difference in measurement time of year (seasonality), time of day, stream temperature, or streamflow to explain the meandering bias shifts in pH over the period of the project.

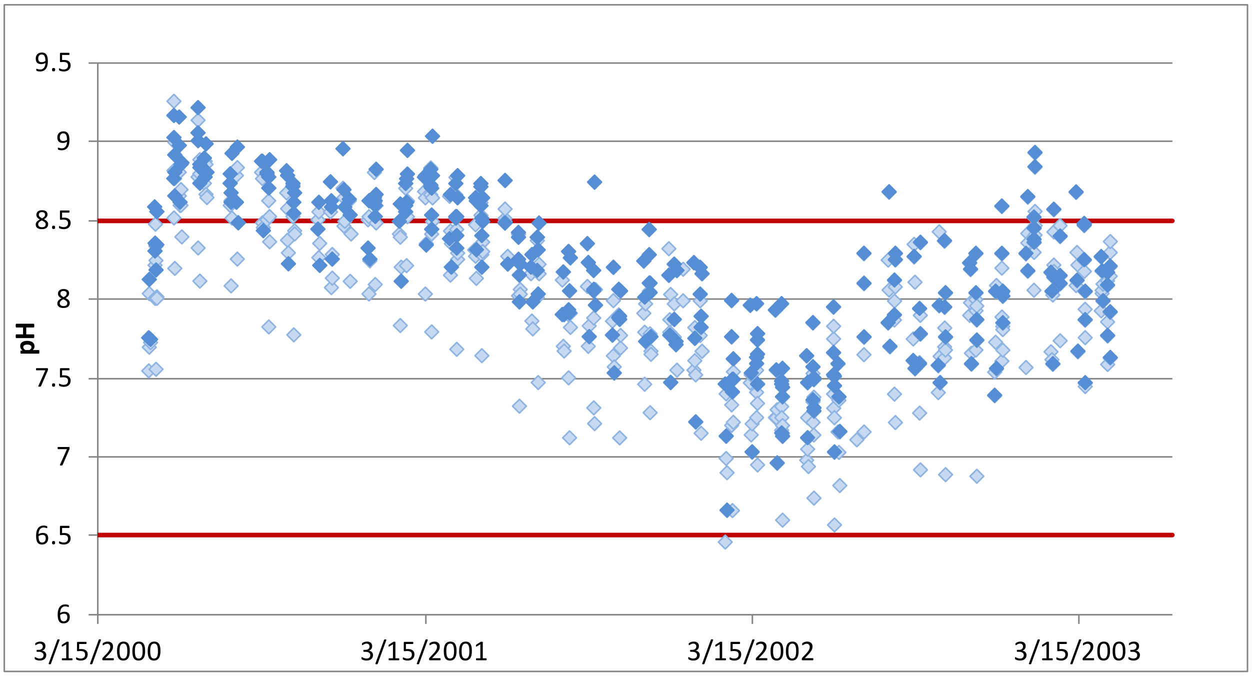


Figure 2. Time-series plot of all pH measurements made by the Okanogan CD for the grant project (#G0000225) in comparison to pH criteria of 6.5 to 8.5.

Verification monitoring

Because of the concerns with the previous monitoring, Ecology re-monitored all 11 tributaries that are on the 303(d) list for verification of pH criteria exceedances. For the tributaries that had more than one segment with pH exceedances, the top-ranked segment of the two (most likely to have higher pH based on earlier monitoring) was re-monitored. Regardless of the time period or any potential bias, some segments consistently had higher pH measurements than other segments during each monthly survey of the previous monitoring project. Table 1 presents a ranking of the segments by the tendency to have a higher pH based on the 2000-2003 monitoring.

The tributary sites that were targeted for re-monitoring are shown on Figure 3. Table 2 lists the latitude and longitude, and the site identification used in Ecology's Environmental Information Management database (EIM) system. The site IDs were established by the original monitoring project by the Okanogan CD. Two new sites were established for this study for Siwash and Tonasket Creeks in August and October 2015 because the original sites were dry. Also a new site was established for the upper Sinlahekin Creek site further downstream from Connors Lake.

Table 1. 303(d)-listed tributaries for pH impairment (by segment) ranked in order of having higher pH measurements during the 2000-2003 monitoring project.

Highlighted segments were draft selections for re-monitoring for the verification study.

Rank	303(d)-Listed Stream Segment for pH Impairment
1	Siwash Creek (lower)
2	Tonasket Creek (lower)
3	Antoine Creek (lower)
4	Johnson Creek (lower)
5	Tunk Creek (lower)
6	Bonaparte Creek (lower)
7	Tonasket Creek (upper)
8	Ninemile Creek (upper)
9	Tallant Creek (upper)
10	Chiliwist Creek (lower)
11	Tunk Creek (upper)
12	Bonaparte Creek (upper)
13	Ninemile Creek (lower)
14	Siwash Creek (upper)
15	Johnson Creek (upper)
16	Tallant Creek (lower)
17	Loup Loup Creek (lower)
18	Sinlahekin Creek (upper)

Table 2. Final tributary sites for the pH verification study in the Okanogan River basin.

Site ID in EIM	Station Description	Latitude	Longitude
LOWERSIWASHCR	Siwash Creek (lower)	48.71158	-119.436
LOTONASKETCR	Tonasket Creek (lower)	48.94322	-119.413
LOWERANTOINECR	Antoine Creek (lower)	48.75903	-119.409
LOWERJOHNSONCR	Johnson Creek (lower)	48.50214	-119.505
LOWERTUNKCR	Tunk Creek (lower)	48.55248	-119.465
LOBONAPARTECR	Bonaparte Creek (lower)	48.70033	-119.439
LONINEMILECR	Ninemile Creek (lower)	48.97075	-119.418
UPPERTALANTCR	Tallant Creek (upper)	48.35772	-119.704
LOCHILIWISTCR	Chiliwist Creek (lower)	48.26689	-119.734
LOLOUPLOUPCR	Loup Loup Creek (lower)	48.28342	-119.708
UPSINLAHEKINCR2	Downstream of Sinlahekin Creek (upper)	48.79060	-119.647
LOWERSIWASHCR2	Upstream of Siwash Creek (lower)	48.71653	-119.384
LOTONASKETCR2	Upstream of Tonasket Creek (lower)	48.94923	-119.381

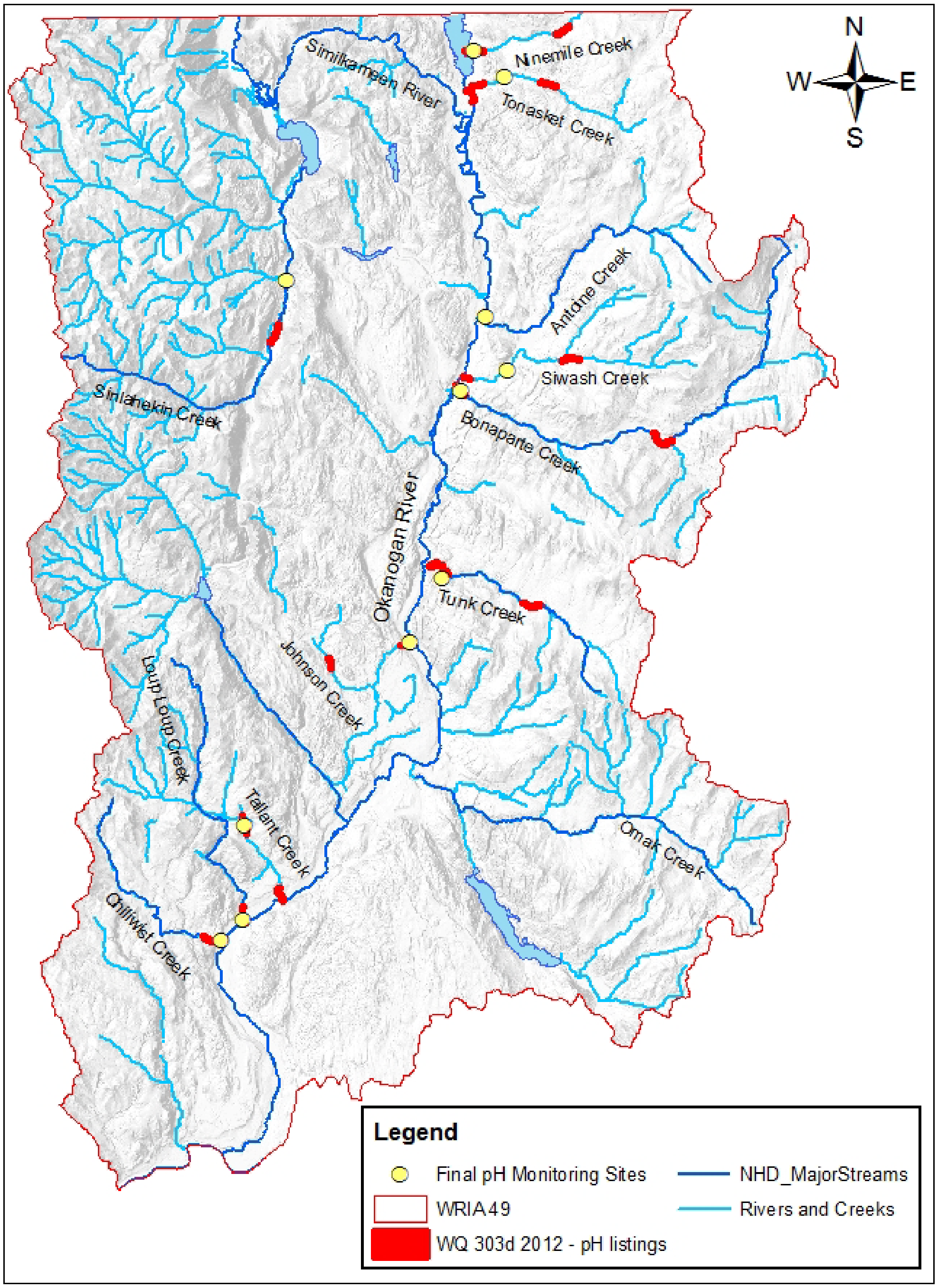


Figure 3. Final sites for verification of pH impairment in the Okanogan River basin.

Methods

Field methods

The study plan was constructed to verify whether there are exceedances of pH water quality standards in selected tributary segments in the Okanogan River basin. The goals of this study were to:

1. Collect pH diel data from select tributaries that are representative of having impaired pH waters based on historical monitoring.
2. Use the collected pH data to determine if pH exceedances are present.
3. Write a summary report that recommends appropriate follow-up actions.

Field methodology for this verification study was outlined in the *Quality Assurance Project Plan: Okanogan River Tributaries 303(d) pH Listings Verification Study* (Carroll, 2015).

In most tributaries, continuous pH was measured in situ for 24 hours, every 30 minutes with a pH data logger to determine the daily minimum and maximum pH at each site. Monitoring events were spread out over three time periods that represented critical conditions to meet minimum requirements for a 303(d) listing assessment.

Use of a pH model to calculate pH saturation

A pH model was used to calculate the pH saturation potential for the Okanogan River tributaries if their measured verification pH levels were above the upper criterion of 8.5 pH units. Appendix B describes the pH model. The model needs four model inputs to calculate the pH saturation:

- water temperature
- specific conductivity
- alkalinity
- concentration of CO_2 in the atmosphere

The pH model was also used to calculate the pH saturation of three tributaries which were sampled for alkalinity in 2000-2003 by the Okanogan CD.

Results

All data collected for the verification study can be found in Ecology's Environmental Information Management database (EIM) which can be accessed on the Ecology website. The study ID used in the EIM system is JICA0003.

Quality assurance results

Of verification data

Appendix A contains the quality assurance (QA) assessment of pH, conductivity and dissolved oxygen (DO) field measurements made for this study. All pH, specific conductance, and DO sensors used in the study had acceptable pre- and post-calibration results, meeting the measurement quality objectives established to meet the project goals.

Of data inputs for pH saturation model

A summary of data inputs used for the pH saturation model is presented in Table 3.

Table 3. Data quality assessment of inputs for pH saturation model.

Data Set	Source	Years	Peer Review / QC?	Approved QAPP?	Formal SOPs?	Comments
Water Temperature	OCD	2000-03	No	Yes	Yes	No QA records
	ECY	2015-16	Yes	Yes	Yes	
Specific Conductivity	OCD	2000-03	No	Yes	Yes	No QA records
	ECY	2015-16	Yes	Yes	Yes	
Alkalinity	OCD	2000-03	No	Yes	Yes	Duplicates analyzed see Appendix C
	ECY	2015-16	See Appendix C	Yes	Yes	Used regression of alkalinity and conductivity
CO_2 Concentration in Atmosphere	NOAA	2000-16	Yes	Yes	Yes	Mauna Loa Observatory

Unk: Unknown
QC: Quality Control
QAPP: Quality Assurance Project Plan
SOPs: Standard Operating Procedures
OCD: Okanogan Conservation District
ECY: Washington State Department of Ecology
NOAA: National Oceanic and Atmospheric Administration

Ancillary field measurements

Streamflow

Streamflows during the 2015 monitoring periods were very low (Table 4), especially due to the drought, but the mean flow in the tributaries are very low most years. The U.S. Geological Survey (USGS) has year-round streamflow gaging in several tributaries: Ninemile, Antoine, Bonaparte, Johnson, and Loup Loup Creeks.

Appendix G shows the USGS flow during the three verification monitoring periods for each creek. Note that the median flow from Antoine Creek shows typical, very low summer and fall flow. Several stations show daily irrigation withdrawal patterns, particularly Antoine Creek, which went dry during part of each day in August 2015.

USGS did a study in 2008 (USGS, 2009) on Tonasket, Antoine, Bonaparte and Tunk creek basins to look at groundwater and surface water interactions. The study found that there was very limited groundwater storage potential in the Tonasket and Antoine creek basins. Coupled with the unconsolidated alluvium under the streambed, these creeks would be expected to have very low flow and most likely go dry in some reaches during the late summer and fall, especially near their mouths.

USGS (2009) found that Bonaparte and Tunk creek basins had more extensive and thicker unconsolidated deposits in their basins and were expected to have a little more potential for base flow in the late summer and fall, although stream losses were again expected near their mouths with the Okanogan River.

Table 4. Estimated and gaged streamflow (cfs) for 2015-2016 verification sites.

Station Description	August 2015	October 2015	April 2016
Tonasket Creek (lower)	dry	dry	≈ 2 − 3
Upstream of Tonasket Creek (lower)	≈ <0.5 seep	≈ <0.5 seep	NA
Antoine Creek (lower)*	0 – 0.3	0 – 0.8	12 – 18
Ninemile Creek (lower)*	0.2	0.2	6 − 7
Tallant Creek (upper)	≈ 2-3	≈ 2-3	≈ 3-4
Loup Loup Creek (lower)*	< 0.5	< 1	100
Bonaparte Creek (lower)*	< 0.5	< 1	28 – 34
Siwash Creek (lower)	dry	dry	≈ 1 − 2
Upstream of Siwash Creek (lower)	≈ <2	≈ <1	NA
Johnson Creek (lower)*	1	0.5	8 – 10
Tunk Creek (lower)	≈ <1	≈ <1	≈ 50
Chiliwist Creek (lower)	≈ <2	≈ <2	≈ 2 − 3
Sinlahekin Creek (upper)	≈ 2 – 3	≈ 2 – 3	≈ >100

*Station streamflow gaged by the USGS.

Specific conductivity

Specific conductivity was measured along with pH in all of the tributaries. In general, conductivities were high, reflecting a high concentration of dissolved minerals (Table 5).

The highest conductivity was in Tonasket Creek and was measured directly from emergent groundwater seeps. Most of the August and October conductivities were higher than the April conductivities, which were diluted by fresh snowmelt runoff.

The variances over 24-hour periods were very low, with the exception of Chiliwist Creek in August 2015 which seemed to have an addition of low ionic water during the monitoring period. All of the other tributaries had consistent source water based on the stable conductivities during each monitoring period.

Table 5 indicates conductivities of tributaries that had verification pH monitoring over the 8.5 upper criterion in bold. Except for Chiliwist Creek, the range of conductivity for these tributaries was from 245 to 568 umhos/cm. Based on a regression of alkalinity and conductivity, pH saturation potential is predicted to be higher than 8.5 pH units whenever specific conductivity is higher than about 340 umhos/cm (see section below on pH modeling).

Table 5. Summary of minimum and maximum measured specific conductivities (umhos/cm) for verification stations.

Station Description	August 2015	October 2015	April 2016
Tonasket Creek (lower)	dry	dry	382 – 413
Upstream of Tonasket Creek (lower)	1074 – 1097	1214 – 1220	NA
Antoine Creek (lower)	665 – 738	641 – 732	245 – 251
Ninemile Creek (lower)	803 – 827	798 – 805	177 – 213
Tallant Creek (upper)	212 – 322	368 – 370	241 – 243
Loup Loup Creek (lower)	304 – 309	293 – 297	156 – 159
Bonaparte Creek (lower)	570 – 585	450 – 525	267 – 275
Siwash Creek (lower)	dry	dry	**408 – 415**
Upstream of Siwash Creek (lower)	606 – 610	607 – 615	NA
Johnson Creek (lower)	**561**	**485 – 516**	**712 – 717**
Tunk Creek (lower)	372 – 385	**433 – 436**	114 – 145
Chiliwist Creek (lower)	**122 – 412**	**391 – 396**	**390 – 396**
Sinlahekin Creek (upper)	**245 – 253**	NA	165 – 171

Verification pH data summary

Table 6 presents a summary of the daily minimum and maximum pH levels recorded at the tributary sites during the pH verification study. Many tributaries had pH levels that met the pH criteria for all 3 verification periods.

Siwash and Tunk Creeks did have pH levels exceeding criteria during one of the verification periods. Johnson, Chiliwist, and Sinlahekin Creeks had pH levels exceeding criteria in two of the verification periods. None of the tributaries exceeded pH criteria for all three periods.

For waters with pH exceeding criteria, Ecology is required to demonstrate how much of the pH exceedance is due to natural conditions and how much is due to anthropogenic activities. Individual assessment of each tributary exceeding criteria is presented in a section below.

Table 6. Summary of pH monitoring results (maximum and minimum) for each tributary site monitored for the verification study.

Tributary Station Site	August 2015		October 2015		April 2016	
	minimum pH	maximum pH	minimum pH	maximum pH	minimum pH	maximum pH
Tonasket Creek (lower)	dry	dry	dry	dry	8.14	8.39
Upstream of Tonasket Creek (lower)	7.15	7.21	7.22	7.32	NA	NA
Antoine Creek (lower)	8.24	8.33	8.25	8.43	8.24	8.36
Ninemile Creek (lower)	8.29	8.39	8.15	8.20	8.16	8.28
Tallant Creek (upper)	7.80	7.96	7.80	7.90	7.69	7.78
Loup Loup Creek (lower)	8.15	8.43	8.09	8.20	7.60	7.85
Bonaparte Creek (lower)	8.23	8.42	8.26	8.37	7.96	8.17
Siwash Creek (lower)	dry	dry	dry	dry	8.47	**8.63**
Upstream of Siwash Creek (lower)	7.66	7.75	7.37	7.44	NA	NA
Johnson Creek (lower)	8.28*	8.28*	**8.53**	**8.63**	**8.50**	**8.62**
Tunk Creek (lower)	7.31	7.43	8.40	**8.55**	7.96	8.02
Chiliwist Creek (lower)	8.27	**8.62**	8.00	8.12	**8.55**	**8.62**
Sinlahekin Creek (upper)	7.96	**8.75**	8.17	**8.55**	7.87	7.97

*Diel data not available for this site, so results are from instantaneous readings.

Use of a pH model to calculate pH saturation

Evaluation of Okanogan CD monitoring data

The model was first used to calculate the pH saturation in three tributaries monitored by the Okanogan CD from 2000-2003. Water temperature, specific conductivity and alkalinity were measured by the Okanogan CD in Bonaparte, Tunk, and Sinlahekin Creeks monthly. The atmospheric concentration of CO_2 was assumed to be 375 ppm in the early 2000s (see Appendix B).

Figure 4 shows the comparison of the pH data measured by the Okanogan CD and the calculated pH saturation data. While the saturated pH remains rather constant between 8.4 and 8.7 pH units, the measured pH data has a meandering bias throughout the monitoring period. Most of the pH measurements from June to October 2000 were above saturation, while later periods show declining levels of under-saturated pH.

The comparison supports the premise that the Okanogan CD pH data has a uniform bias, most likely caused by a failing pH sensor. This conclusion corroborates the data quality assessment made earlier that found no correlation between the measured pH and other factors (seasonality, time of day, stream temperature, or streamflow) to explain the meandering bias shifts in pH throughout the 3-year monitoring period.

The Okanogan CD pH data cannot be quality assured because quality control records no longer exist to verify the data quality. Neither the data nor missing quality records were reviewed by Ecology before it was loaded into the EIM database system. Without proper data quality records and with overwhelming evidence that the data are biased, Ecology is left to conclude the data are unusable for a water quality assessment.

The data quality status of the pH data in EIM (known as "Study QA Assessment Level") is currently set to high quality, peer-reviewed data. The status should be changed to unverified data and the pH data should not be used for the water quality assessment.

Evaluation of pH saturation potential above criteria

The calculated pH saturation in the three tributaries is often above the Washington State upper pH criterion of 8.5 pH units (Figure 4). The average conductivity in the three tributaries was 438 umhos/cm and the average alkalinity was 166 mg/L as $CaCO_3$.

The model shows that the pH saturation is very sensitive to alkalinity. Figure 5 shows the relationship between alkalinity in freshwater and the calculated pH saturation. This relationship used a ratio of alkalinity to conductivity of 0.37, the same as found in measured Okanogan basin data (see below).

When the alkalinity in freshwater, a natural characteristic of the basin's geo-chemistry, is greater than 125 mg/L as $CaCO_3$, then the pH saturation is expected to exceed the upper criterion of 8.5 pH units.

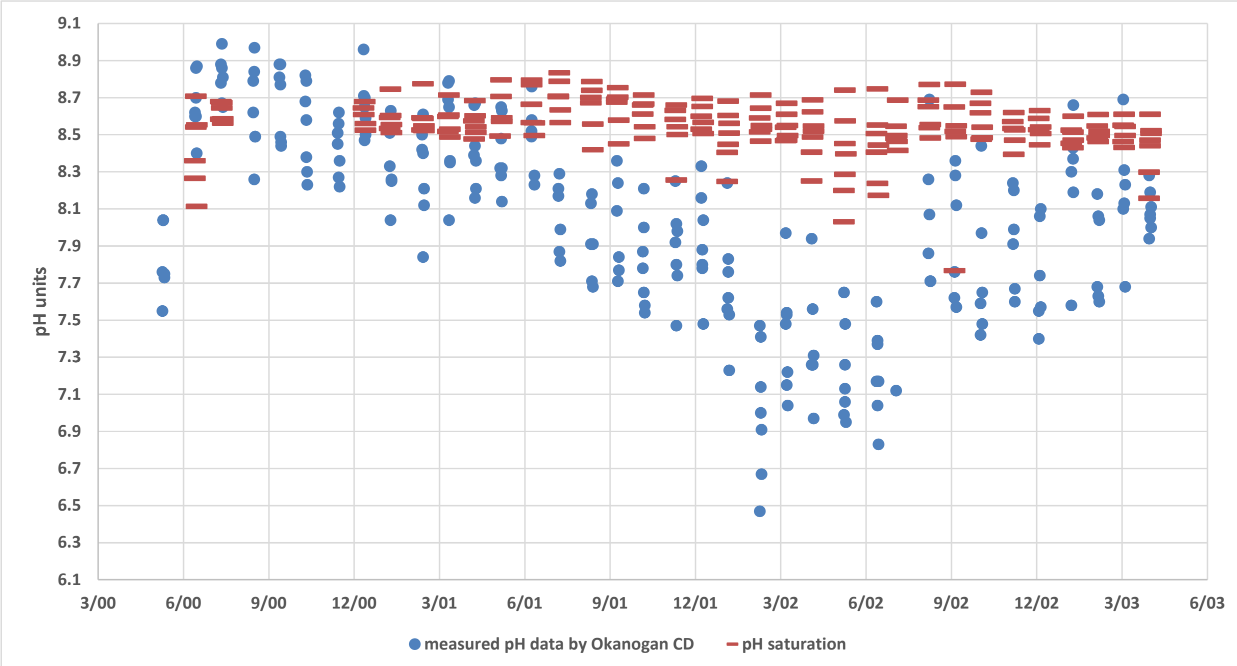


Figure 4. Comparison of measured pH data by the Okanogan CD in three tributaries and the calculated pH saturation in the same tributaries.

No alkalinity data were collected in late 2000.

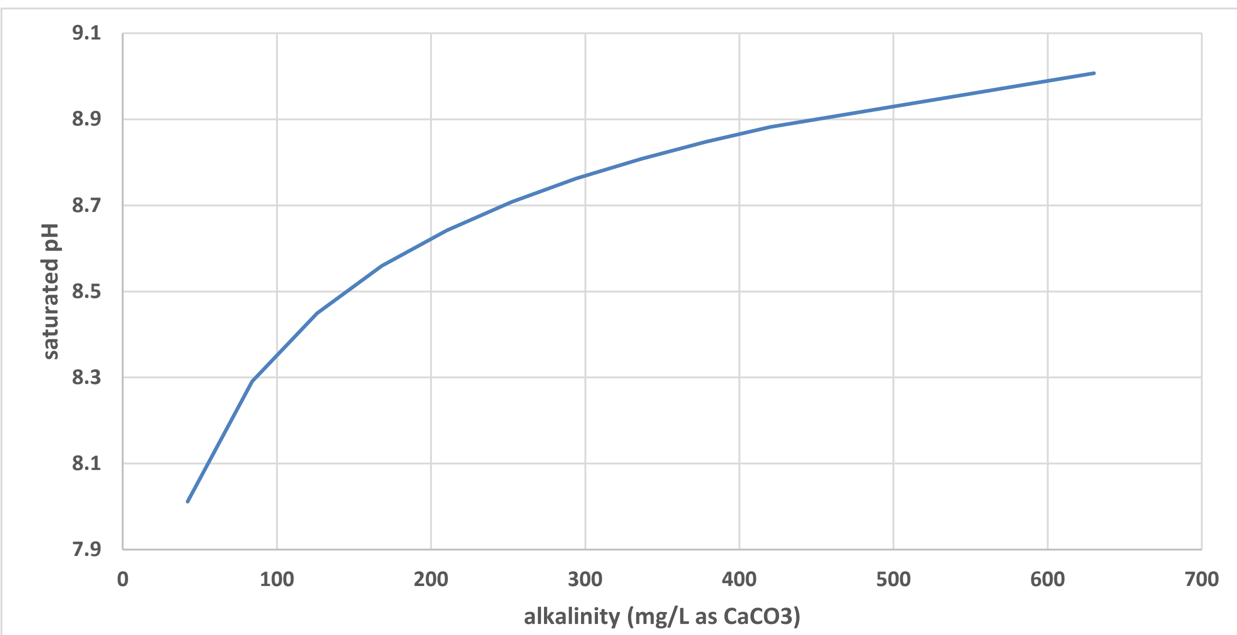


Figure 5. Calculated pH saturation relationship to alkalinity in Okanogan River tributaries.

Evaluation of verification pH data

Saturated pH levels were also estimated for verification sites with pH levels over the upper criterion of 8.5 pH units (results are in section below by location). Alkalinity had to be estimated because it was not measured during the verification study. Previous measurements of alkalinity by the Okanogan CD in three tributaries and a regression of alkalinity to conductivity were used to estimate the alkalinity (Appendix C).

A comparison of verification pH data and estimated pH saturation was used to tell if pH in the stream was being influenced by biological activity, and thus have potential for anthropogenic impacts.

This study determined if pH in a tributary stream was being influenced by biological activity by comparing the difference in diel amplitudes of the pH saturation and observed verification pH time series. If the diel amplitude difference between the two was 0.10 pH units or less, then the tributary was considered to have de minimis biological activity and to be in equilibrium with the saturation potential throughout the day. A pH change of 0.10 or less is also equated with a change having no measurable effect. The de minimis evaluation is only possible when diel data (time series) is available at a site.

Sometimes the observed pH was below saturation but still constant throughout the day (very little diel amplitude) mimicking the relative amplitude of saturated pH levels. This was also considered an equilibrium condition as long as the difference in amplitudes was 0.10 pH units or less.

Presence of a diel amplitude difference greater than 0.10 pH units (often with pH values above pH saturation in the afternoon and below pH saturation at night) indicated biological activity influencing the pH of the stream. Some biological activity is normal in most sunlit streams. Separating natural productivity from productivity induced by nutrient enrichment is sometimes difficult to do, usually requiring a more intensive study to determine the source of the nutrients. Determining nutrient enrichment from anthropogenic sources was outside the scope of this present verification study.

Verification pH data results by location

The study design for this verification study incorporated the following decision-making criteria for verifying exceedances of the pH water quality standards in the Okanogan River tributaries:

- If any of the tributaries showed no pH exceedances for all three verification re-monitoring periods, then this study would be satisfied that the entirety of that tributary is not exceeding pH standards, including secondary segments listed for pH exceedances that were not re-monitored. A recommendation would be made for delisting all segments attributed to those tributaries.
- If re-monitored segments showed pH exceedances only once or twice during the three verification re-monitoring periods, then this study would evaluate how impaired those specific sites were and if they represented the overall condition of the whole tributary. The study may recommend more monitoring to characterize the potential impairment.

- If a re-monitored segment showed pH exceedances during all three verification re-monitoring events, then this study would most likely determine that there was an overall potential for pH impairment in the entirety of that tributary and a TMDL study would be recommended for that tributary.

Verification monitoring showing no pH exceedances

There were six tributaries that fell into the first category where all three of the verification monitoring periods showed no pH exceedances. Based on the results and the decision-making criteria, the verification monitoring sites on Tonasket, Antoine, Ninemile, Tallant, Loup Loup, and Bonaparte Creeks are all recommended to be delisted for pH from the 303(d) list.

In addition, other listed reaches on Tonasket, Ninemile, Tallant, and Bonaparte Creeks that were not re-monitored during the verification study are also recommended to be delisted because the verification study used the monitored sites as proxies for the verification of all other reaches on the same tributaries. Table 7 summarizes the listings recommended for delisting.

Table 7. Okanogan River tributary segments that are recommended to be delisted from the 2012 303(d) list for showing no pH exceedances as a result of the verification study.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Tonasket Creek	41831	1194229489371	1.64	0.00
Tonasket Creek	50595	1194229489371	8.90	7.34
Antoine Creek	41827	1194112487614	0.77	0.00
Ninemile Creek	41326	1194333489670	2.18	0.52
Ninemile Creek	51195	1194333489670	10.92	9.52
Tallant Creek	50616	1196594482977	10.06	7.90
Tallant Creek	50615	1196594482977	1.46	0.00
Loup Loup Creek	41828	1197043482804	1.67	0.00
Bonaparte Creek	41280	1194456487053	1.18	0.00
Bonaparte Creek	50600	1194456487053	24.66	22.11

In addition, there is a new Bonaparte Creek listing for pH on the current 303(d) list, recently approved by EPA. The listing is for a segment reach above the 2012 listing for the reach at the mouth.

Table 8 shows the new pH listing for Bonaparte Creek on the current 303(d) list. The verification study monitored a site very close to the new listing reach. This evaluation recommends using the same decision-making criteria that was used for other un-verified reaches. Specifically, the monitoring site used in the verification study will be a proxy for the verification of all currently listed reaches on the same tributary.

Table 8. Additional Bonaparte Creek segment with pH listing on the current 303(d) list recommended for delisting.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Bonaparte Creek	50599	1194456487053	4.095	2.026

Tonasket Creek

Tonasket Creek has both a lower and upper reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were mainly from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high, as well as the spring of 2003 when all pH measurements were biased high again.

The site in lower Tonasket Creek was dry during the verification surveys in August and October 2015. This was a common summer and fall occurrence during the Okanogan CD monitoring as well. The USGS also found reaches of Tonasket Creek to be intermittent during their 2008 monitoring season (USGS, 2009).

Ecology monitored at the closest accessible sites upstream that still had flowing water for the verification study. The next upstream site was about 2 miles upstream below a road culvert that had groundwater flow coming out of the ground around the culvert. The surfacing groundwater had very low flow (< 1 cfs).

The 303(d)-listed site in upper Tonasket Creek was inaccessible in 2015 due to wildfire in the upper watershed, and was therefore unavailable as a replacement site for the dry lower Tonasket Creek site. Overall, the creek channel was intermittently dry further upstream except for similar groundwater seeps and pools.

The original lower Tonasket Creek site on the Eastside Oroville Road had flowing water in April 2016 and was monitored for the verification study.

All verification pH monitoring on Tonasket Creek showed values below the upper criterion of 8.5 pH units, with springtime pH monitoring having the highest diel range from 8.14 to 8.39 pH units (Figure 6). Based on the decision criteria for this verification study, this study recommends delisting both the lower and upper Tonasket Creek reaches that are on the 303(d) list for pH.

Antoine Creek

Antoine Creek only has one site on the 303(d) list for exceeding the upper criterion of 8.5 pH units. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. Most of the pH exceedances were from the early monitoring in 2000-01 when all the pH data appears to have been biased high.

Antoine Creek had very little flow during the verification study and went dry part of each day during the August 2015 verification re-monitoring. Based on the flow pattern recorded by the USGS flow gage, there is daily irrigation withdrawals on Antoine Creek (Appendix E). USGS (2009) found that the Antoine Creek basin has thin, unconsolidated deposits not capable of storing or producing very much groundwater.

All verification pH monitoring on Antoine Creek showed values below the upper criterion of 8.5 pH units, with all three periods having a consistent diel range between 8.24 and 8.43 pH units (Figure 7). Based on the decision criteria for this verification study, this study recommends delisting the lower Antoine Creek reach that is on the 303(d) list for pH.

Ninemile Creek

Ninemile Creek has both its lower and upper sites on the 303(d) list for pH exceeding the upper criterion of 8.5 pH units. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were from the early monitoring in 2000-01 when all the pH data appears to have been biased high.

The site in upper Ninemile Creek was inaccessible in 2015 due to wildfire in the upper watershed, so the 303(d)-listed lower Ninemile Creek site was used instead for the verification study.

Ninemile Creek had very little flow during the verification study. The lower site is near the mouth where a USGS streamflow gage is stationed. Appendix E shows the USGS streamflow during each of the verification monitoring periods. Ninemile Creek basin is just north of the Tonasket and Antoine Creek basins which USGS (2009) found to have the thin, unconsolidated deposits not capable of storing or producing very much groundwater.

All verification pH monitoring on lower Ninemile Creek showed values below the upper criterion of 8.5 pH units, with all three periods having a consistent diel range between 8.15 and 8.39 pH units (Figure 8). Based on the decision criteria for this verification study, this study recommends delisting both reaches on Ninemile Creek that are on the 303(d) list for pH.

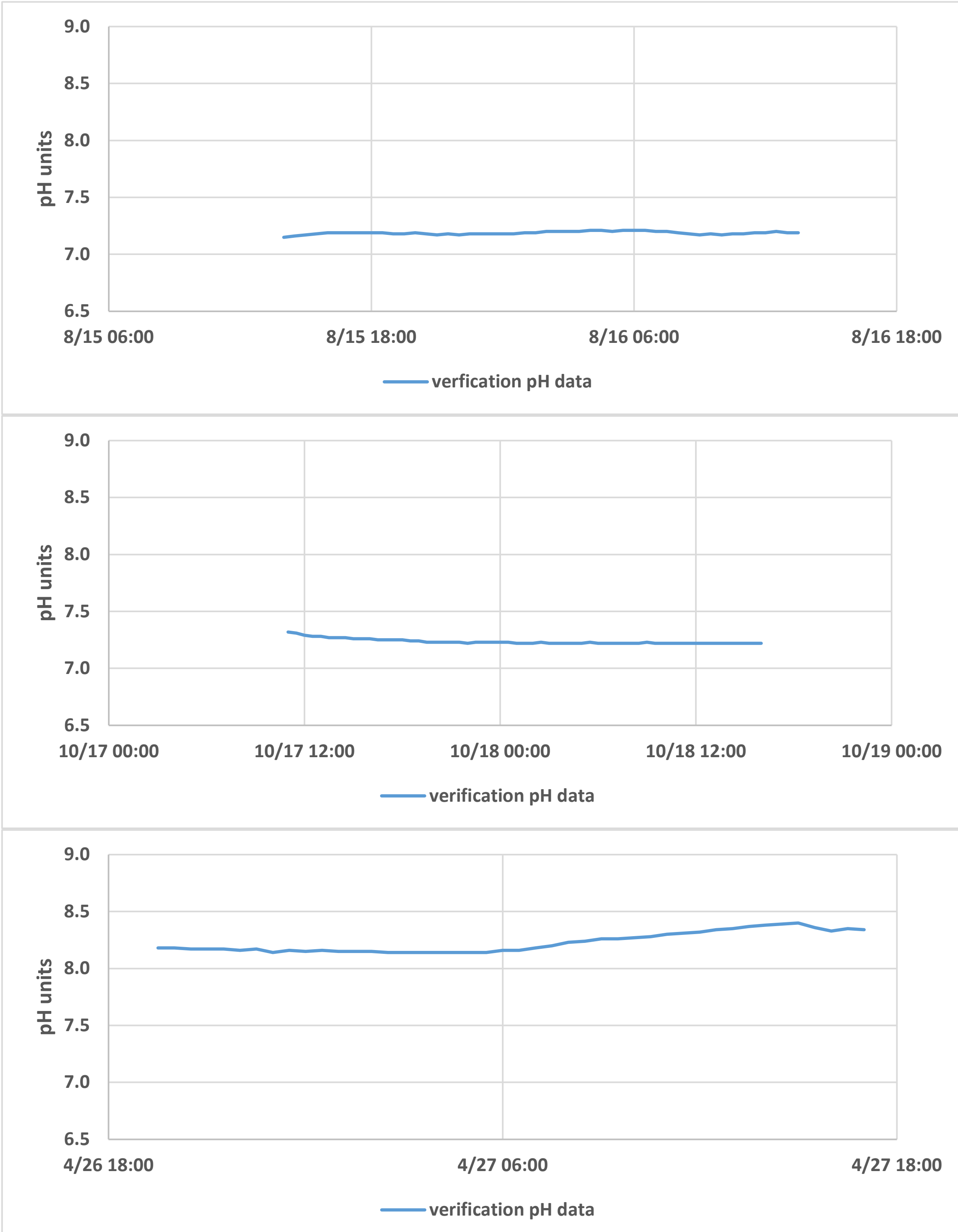


Figure 6. Results of pH time series for Tonasket Creek verification monitoring in August and October 2015 and April 2016.

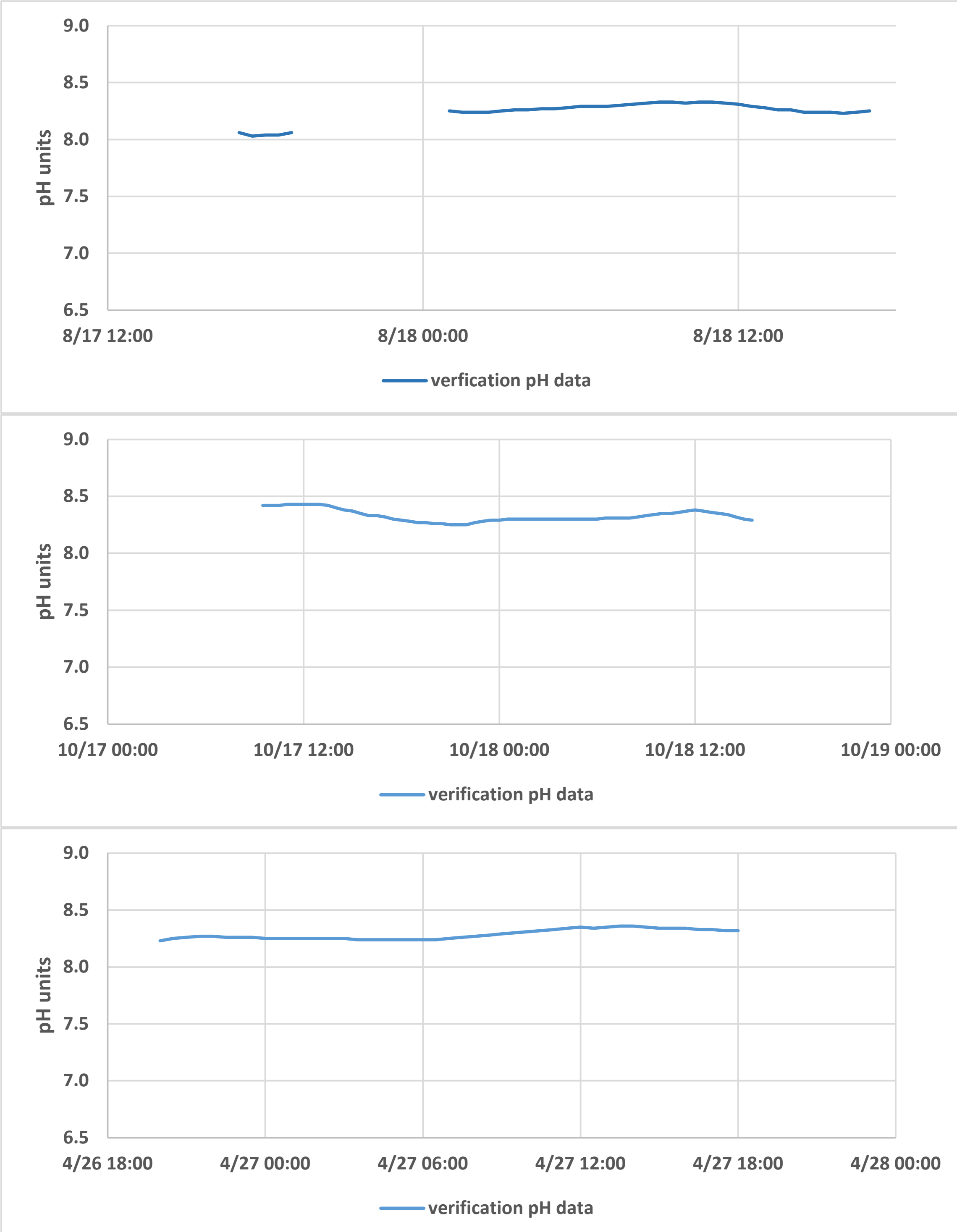


Figure 7. Results of pH time series for Antoine Creek verification monitoring in August and October 2015 and April 2016.

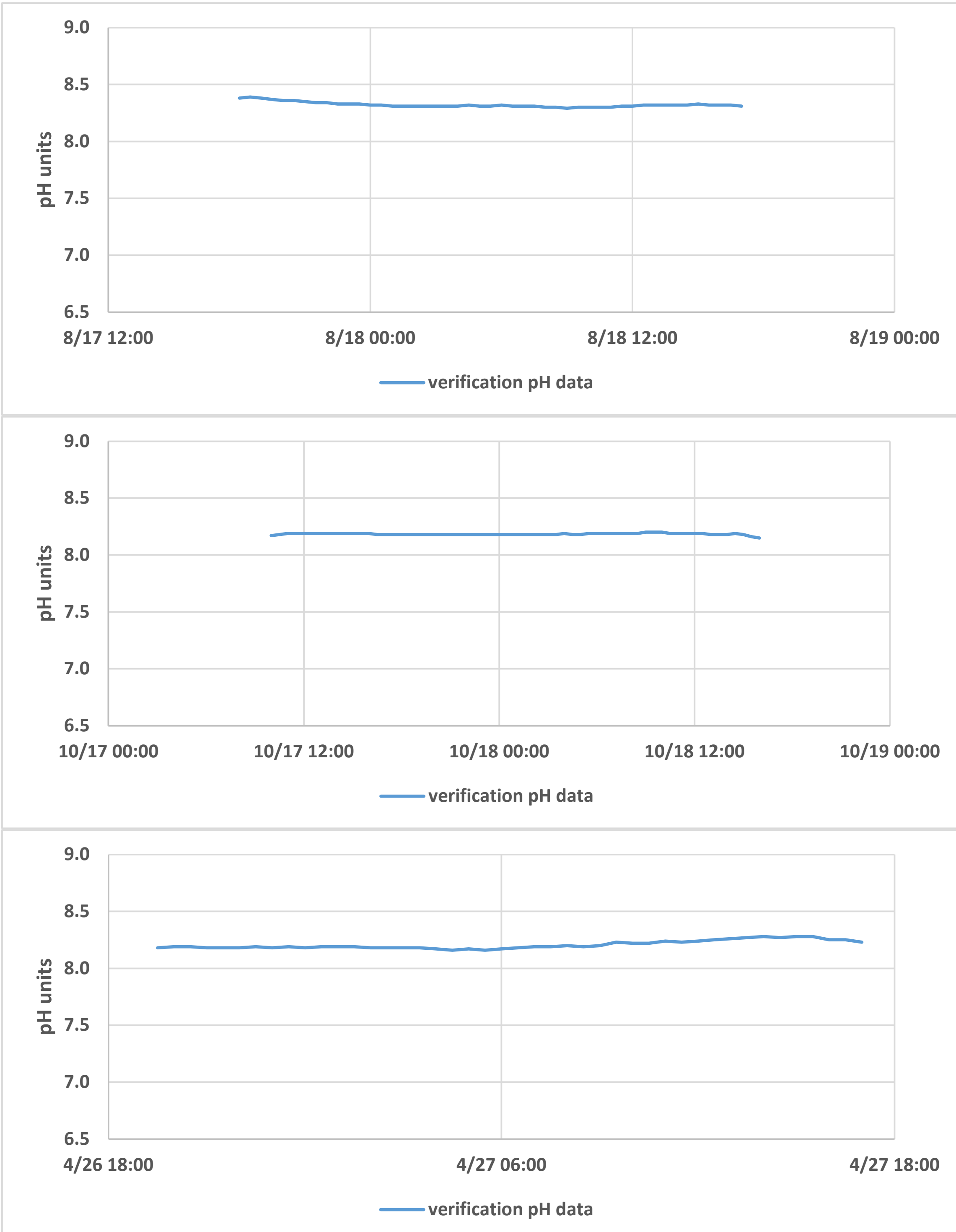


Figure 8. Results of pH time series for Ninemile Creek verification monitoring in August and October 2015 and April 2016.

Tallant Creek

Tallant Creek has both a lower and upper site on the 303(d) list for pH exceeding the upper criterion of 8.5 pH units. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were from the early monitoring in 2000-01 when all the pH data appears to have been biased high.

There were only five pH measurements from May to August 2000 at the lower site in Tallant Creek during the Okanogan CD monitoring presumably because the lower reach of Tallant was dry.

During the verification study, most of the flow in upper Tallant Creek was from the release of water from Leader Lake which is a reservoir for irrigation. The release from the lake is from a gate at the bottom of the reservoir dam. The lake water quality mostly influences the water quality of Tallant Creek; the channel above the Leader Lake inflow was mostly dry.
Tallant Creek is used as a conveyance for irrigation water from Leader Lake to irrigation customers lower in the valley. Irrigation diversions lower in the valley account for the low flows at the lower monitoring site.

All verification pH monitoring in upper Tallant Creek showed values below the upper criterion of 8.5 pH units, with all three periods having a consistent diel range between 7.69 and 7.96 pH units (Figure 9). Based on the decision criteria for this verification study, this study recommends delisting both reaches of Tallant Creek that are on the 303(d) list for pH exceedance.

Loup Loup Creek

Loup Loup Creek has only one site on the 303(d) list for pH exceeding the upper criterion of 8.5 pH units. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were from the early monitoring in 2000-01 when all the pH data appears to have been biased high.

The lower site is near the mouth where a USGS streamflow gage is stationed. Appendix E shows the USGS streamflow during each of the verification monitoring periods.

All verification pH monitoring in Loup Loup Creek showed values below the upper criterion of 8.5 pH units, with the summer and fall periods having a diel range between 8.09 and 8.43 pH units (Figure 10). There was some diel change to the measurements indicating limited biological activity, especially in August, but not enough to exceed the 8.5 upper pH criterion. The springtime runoff had a diel pH range between 7.60 and 7.85 (Figure 10).

Based on the decision criteria for this verification study, this study recommends delisting the lower reach on Loup Loup Creek that is on the 303(d) list for pH.

Bonaparte Creek

Bonaparte Creek has both a lower and upper reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. Most of the pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

All verification pH monitoring on lower Bonaparte Creek showed values below the upper criterion of 8.5 pH units, with the summer and fall periods having a consistent diel range between 8.23 and 8.42 pH units (Figure 11). The springtime runoff had a diel pH range between 7.96 and 8.17 (Figure 11). Based on the decision criteria for this verification study, this study recommends delisting both reaches of Bonaparte Creek that are on the 303(d) list for pH.

Lower Bonaparte Creek is also a basin site for Ecology’s Freshwater Monitoring Unit (FMU) which is monitoring the creek monthly from October 2014 to September 2016. The FMU consistently made measurements of pH above the criteria but most likely introduced a bias due to sampling methodology (Appendix D).

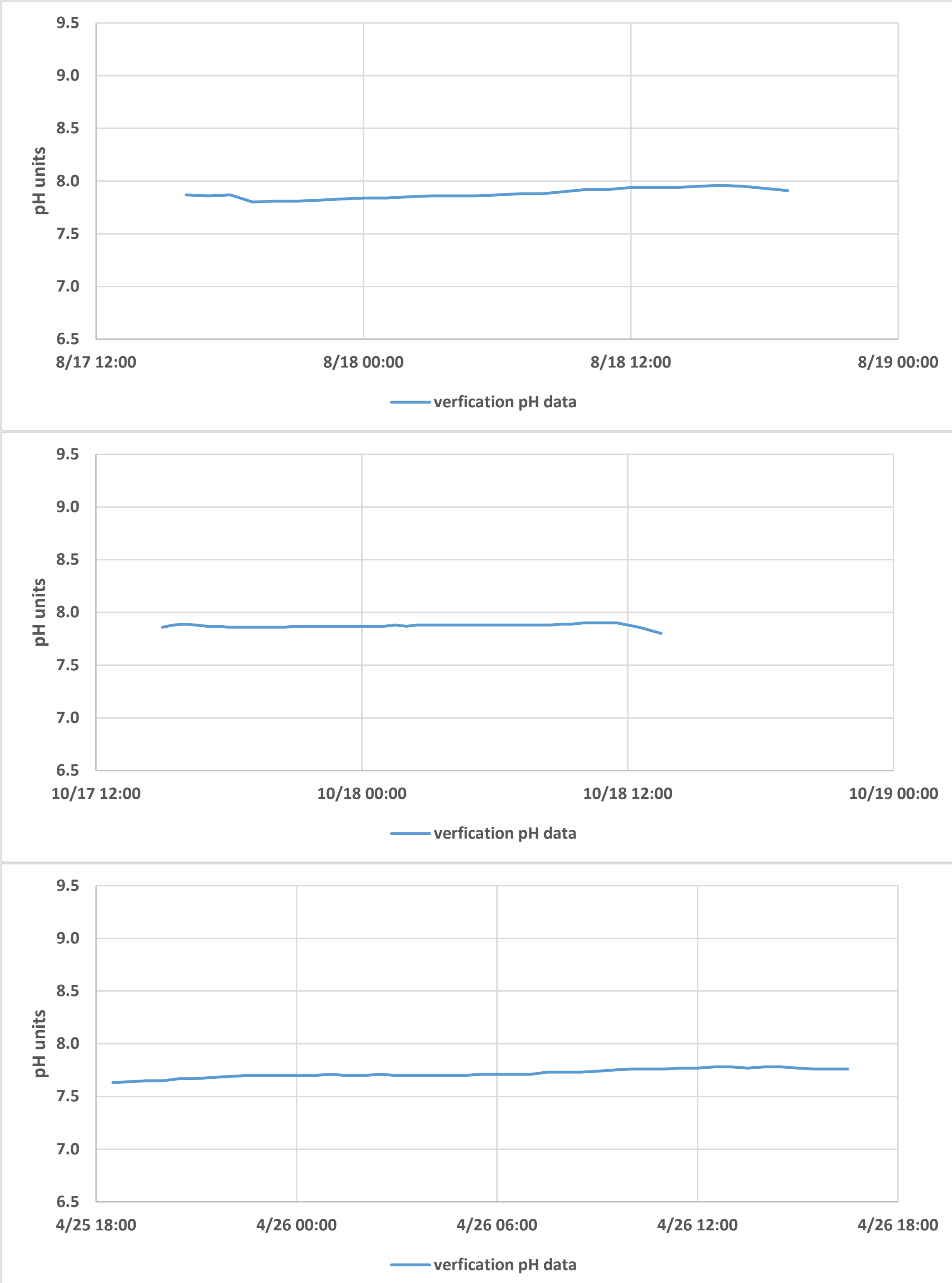
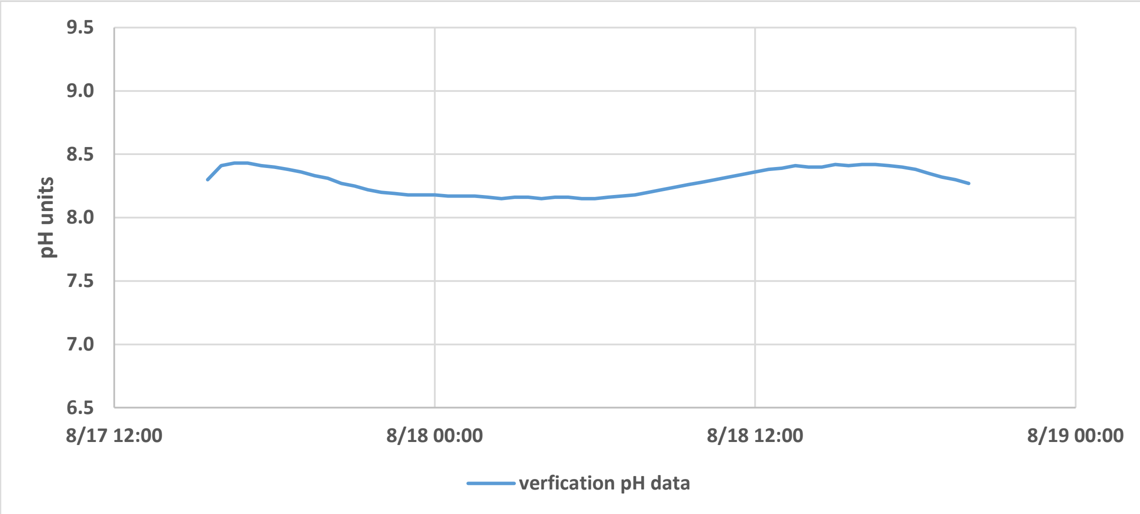
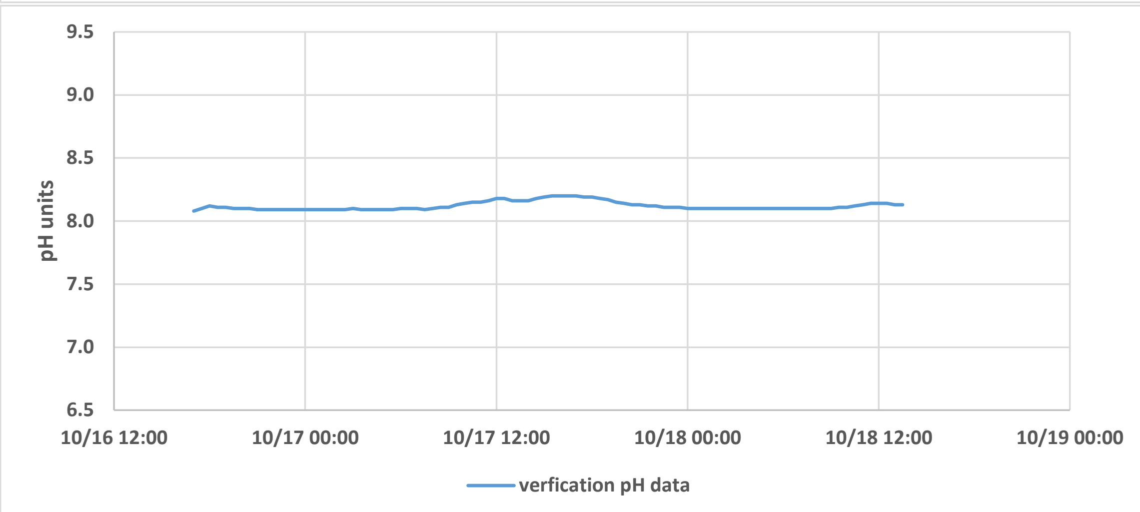


Figure 9. Results of pH time series for Tallant Creek verification monitoring in August and October 2015 and April 2016.





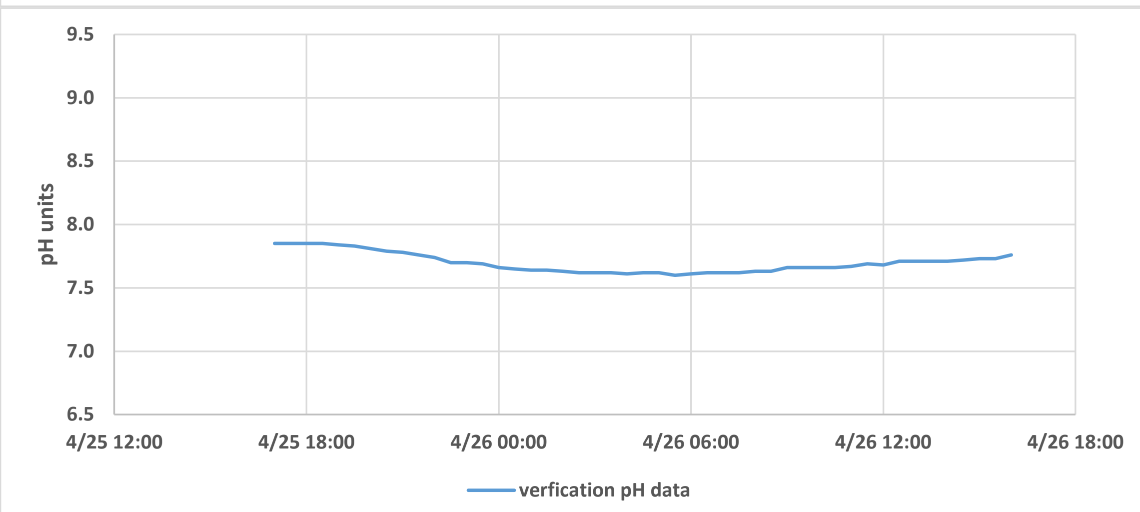


Figure 10. Results of pH time series for Loup Loup Creek verification monitoring in August and October 2015 and April 2016.

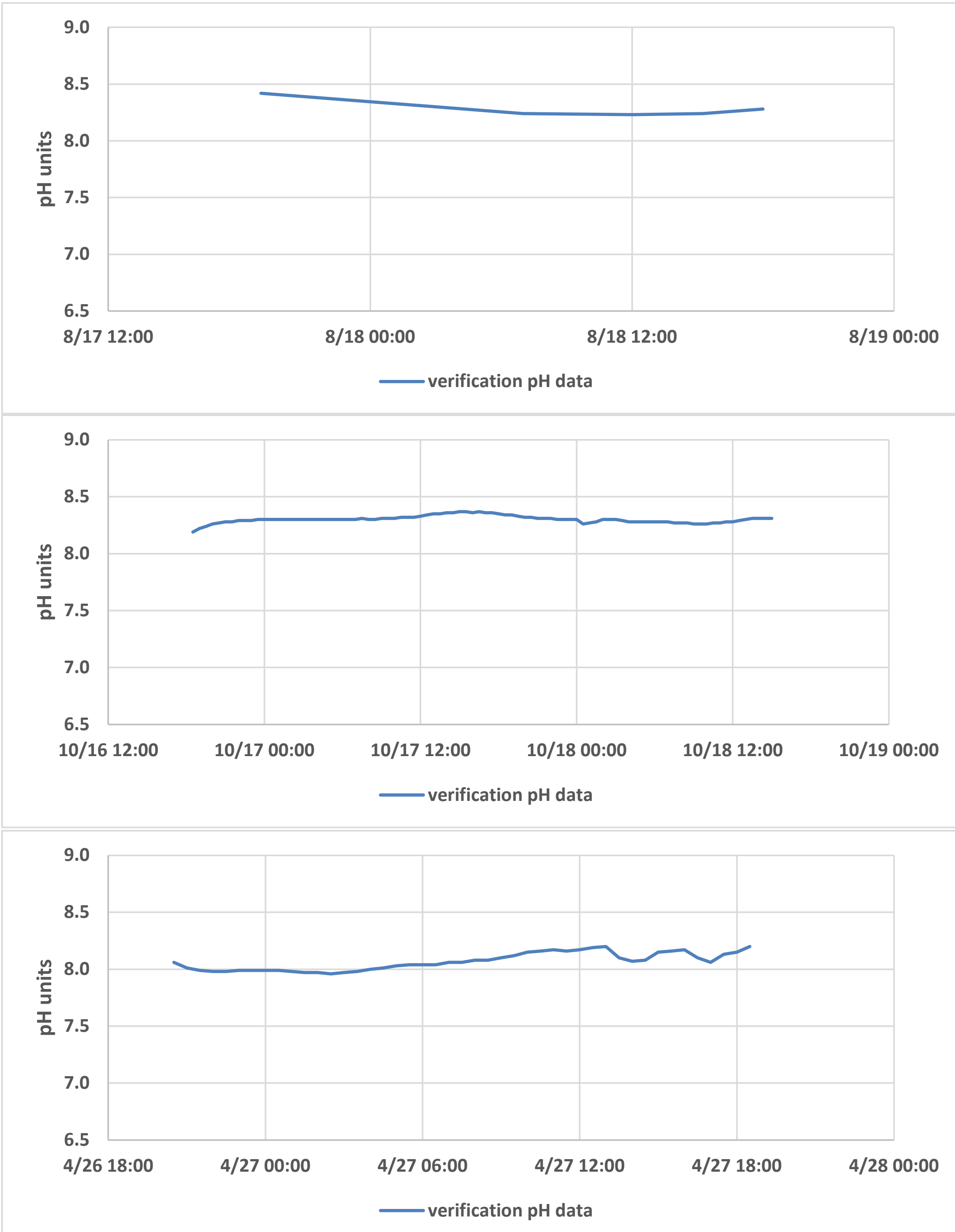


Figure 11. Results of pH time series for Bonaparte Creek verification monitoring in August and October 2015 and April 2016.

Verification monitoring showing exceedances of pH criteria

Several tributaries had verification pH monitoring that exceeded the upper limit criterion of 8.5 pH units during 1 or 2 of the verification monitoring periods. Reaches on lower Johnson, Siwash, and Tunk Creeks and upper Chiliwist and Sinlahekin Creeks fell into this category.

For waters with pH exceeding the criteria, Ecology is required to demonstrate how much of the pH exceedance is due to natural conditions and how much is due to anthropogenic activities. The standards have no allowance for increases in pH from anthropogenic sources if the pH in the stream's natural equilibrium is above 8.5 pH units.

This study determined if pH in a tributary stream was being influenced by biological activity by comparing the difference in diel amplitudes of the pH saturation and observed verification pH time series. If the diel amplitude difference between the two were 0.10 pH units or less, then the tributary was considered to have de minimis biological activity and to be in equilibrium with the saturation potential throughout the day. Table 9 shows the diel amplitude differences for each tributary verification monitoring period for tributaries that exceeded the upper criterion of 8.5 pH units.

Table 9. Amplitude difference between saturation diel pH levels and verification diel pH levels.

Tributary	August 2015	October 2015	April 2016
Siwash Creek	0.03	0.02	0.07
Johnson Creek	NA	0.04	0.03
Tunk Creek	0.06	0.08	0.01
Chiliwist Creek	0.00	0.06	0.02
Sinlahekin Creek	0.33	0.19	0.05

Only Sinlahekin Creek showed potential excessive biological activity in August and October 2015. Some biological activity is normal in most sunlit streams. Separating natural productivity from productivity induced by nutrient enrichment is sometimes difficult to do. A more intensive study is necessary to determine the source of the nutrients.

For each of the tributaries that showed exceedances of pH criteria, the observed verification pH data is compared to the calculated pH saturation below.

Siwash Creek

Siwash Creek has both a lower and upper reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. Most of the pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

The site at lower Siwash Creek was dry during the monitoring surveys in August and October 2015. Monitoring was performed at the next accessible site upstream that still had flowing water. The next upstream site was about 2 miles upstream at Fancher Road. There was a small flow of 1 to 2 cfs at this site in the summer and fall of 2015.

The 303(d)-listed site in upper Siwash Creek was inaccessible in 2015 due to closed roads from wildfire, and was therefore unavailable as a replacement site for the dry lower Siwash Creek site.

The lower Siwash site near the mouth apparently goes dry in most years, with the small amount of flow going subsurface into rocky, unconsolidated deposits below the stream channel. The Okanogan CD monitored the site 10 times, during the spring runoff months of their monitoring years when there was enough streamflow to make it down to the mouth.

The verification monitoring at Fancher Road showed no pH exceedances in August and October 2015 (Figure 12). The creek had very low streamflow (≈ 1-2 cfs) and had high conductivity suggesting groundwater/surface water interaction during this time of year at this location.

During the April 2016, the creek had low flow (≈ 1-2 cfs) at the original lower Siwash Creek site, so the verification monitoring was done at that location. The conductivity was still high (≈ 400 umhos/cm), again suggesting groundwater/surface water interaction.

The pH in April ranged from 8.47 to 8.63, showing a small exceedance above the upper criterion of 8.5 for part of the day (Figure 12). The creek was running clear but was well-shaded and had no appearance of algal or macrophyte growth. The pH saturation for that day was estimated to be 8.54, just above the upper pH criterion. The April pH verification data were essentially at saturation levels during the April 2016 monitoring period (Figure 12).

Based on the diel amplitude differences being less than 0.10 pH units (Table 9), this study is satisfied that the pH exceedance in Siwash Creek is due to the pH levels being at equilibrium to natural saturation conditions and not caused by anthropogenic influences. Accordingly, this study recommends delisting Siwash Creek from the 303(d) list for pH.

Johnson Creek

Johnson Creek has both a lower and upper reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. Most of the pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

Verification pH monitoring on lower Johnson Creek in October 2015 and April 2016 showed values slightly above the upper criterion of 8.5 pH units (Figure 13), having a consistent diel range between 8.50 and 8.71 pH units. The summer August 2015 datalogger failed to take readings, but a single pH check reading on August 18 at 4:30 pm, when maximum daily pH is expected, had a reading of 8.28 pH units.

Based on the diel amplitude differences being less than 0.10 pH units (Table 9), this study is satisfied that the pH exceedance in Johnson Creek is due to pH levels being at or near natural saturation conditions and not caused by anthropogenic influences. Accordingly, this study recommends delisting Johnson Creek from the 303(d) list for pH.

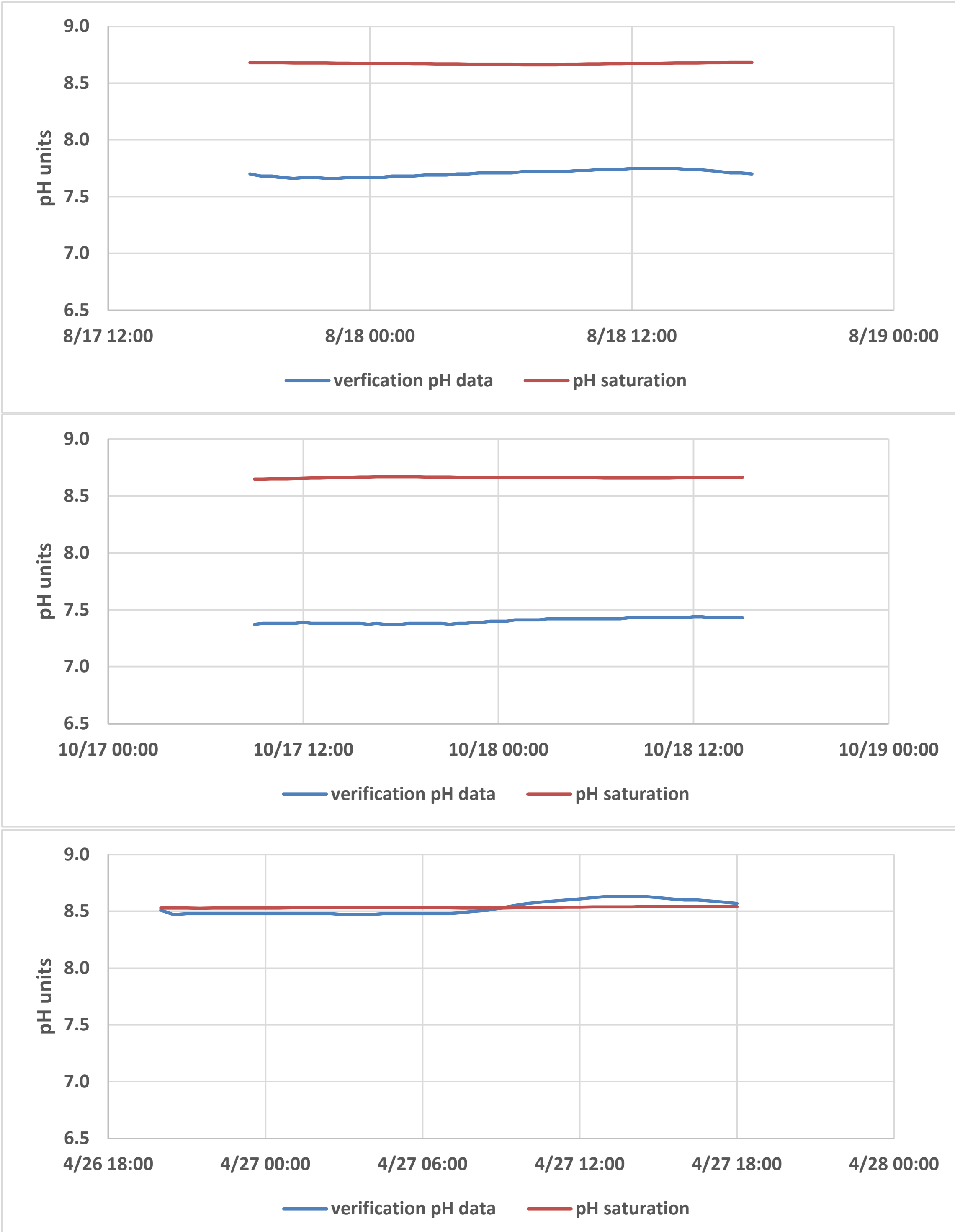


Figure 12. Results of pH time series for Siwash Creek verification monitoring in August and October 2015 and April 2016.

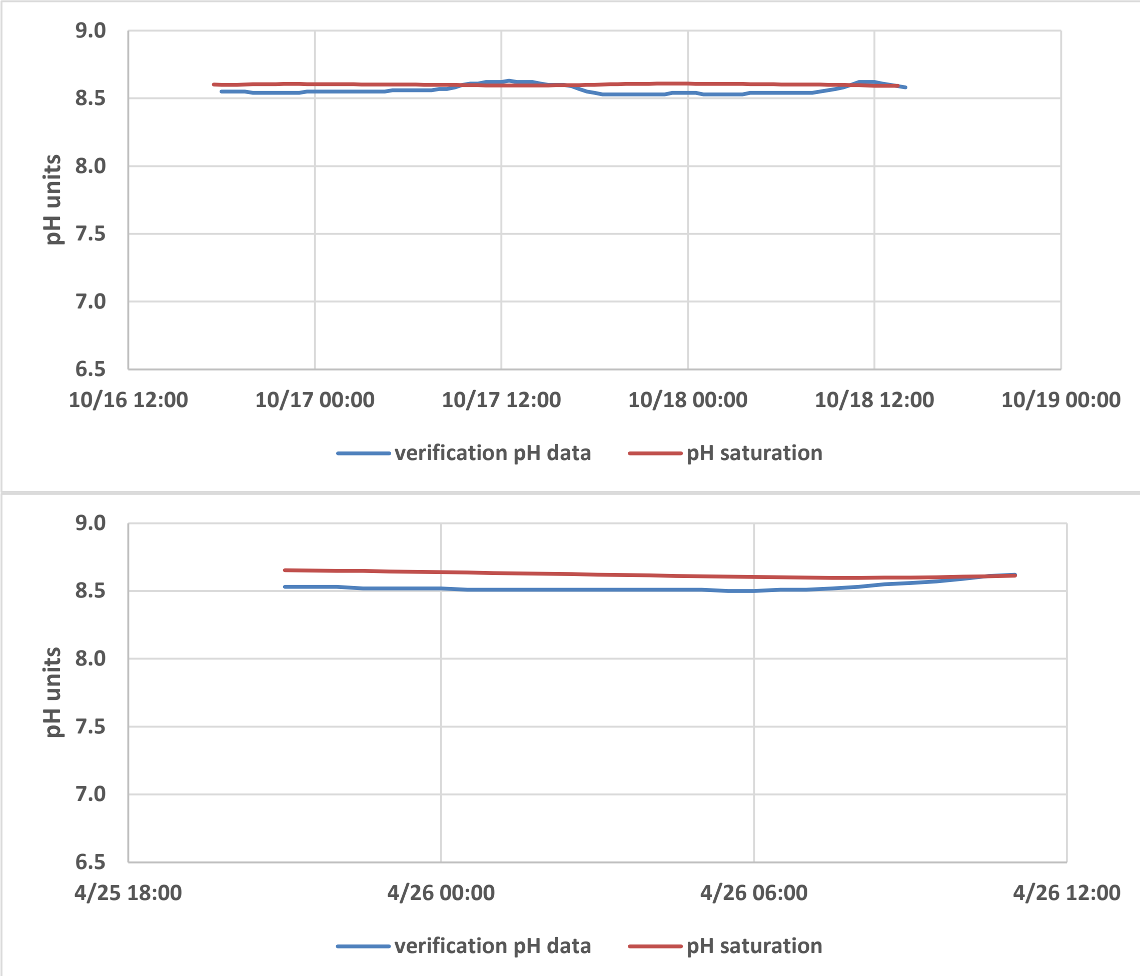


Figure 13. Results of pH time series for Johnson Creek verification monitoring in October 2015 and April 2016.

Tunk Creek

Tunk Creek has both a lower and upper reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

The verification monitoring in lower Tunk Creek showed no pH exceedances in August 2015 and April 2016 (Figure 14). The pH in October ranged from 8.40 to 8.55, showing a small exceedance of the upper criterion of 8.5 for part of the day (Figure 14).

Lower Tunk Creek reach is well-shaded with a fully developed riparian that runs in a fairly steep canyon. The creek had very low flow (≈ <1 cfs) in August and October 2015 and did not appear very productive, maybe because of the shaded conditions. The conductivity of the water was moderately high, suggesting groundwater/surface water interaction. In April 2016 the flow was much higher (≈ 50 cfs) with higher turbidity and lower conductivity reflecting what appeared to be spring-runoff conditions.

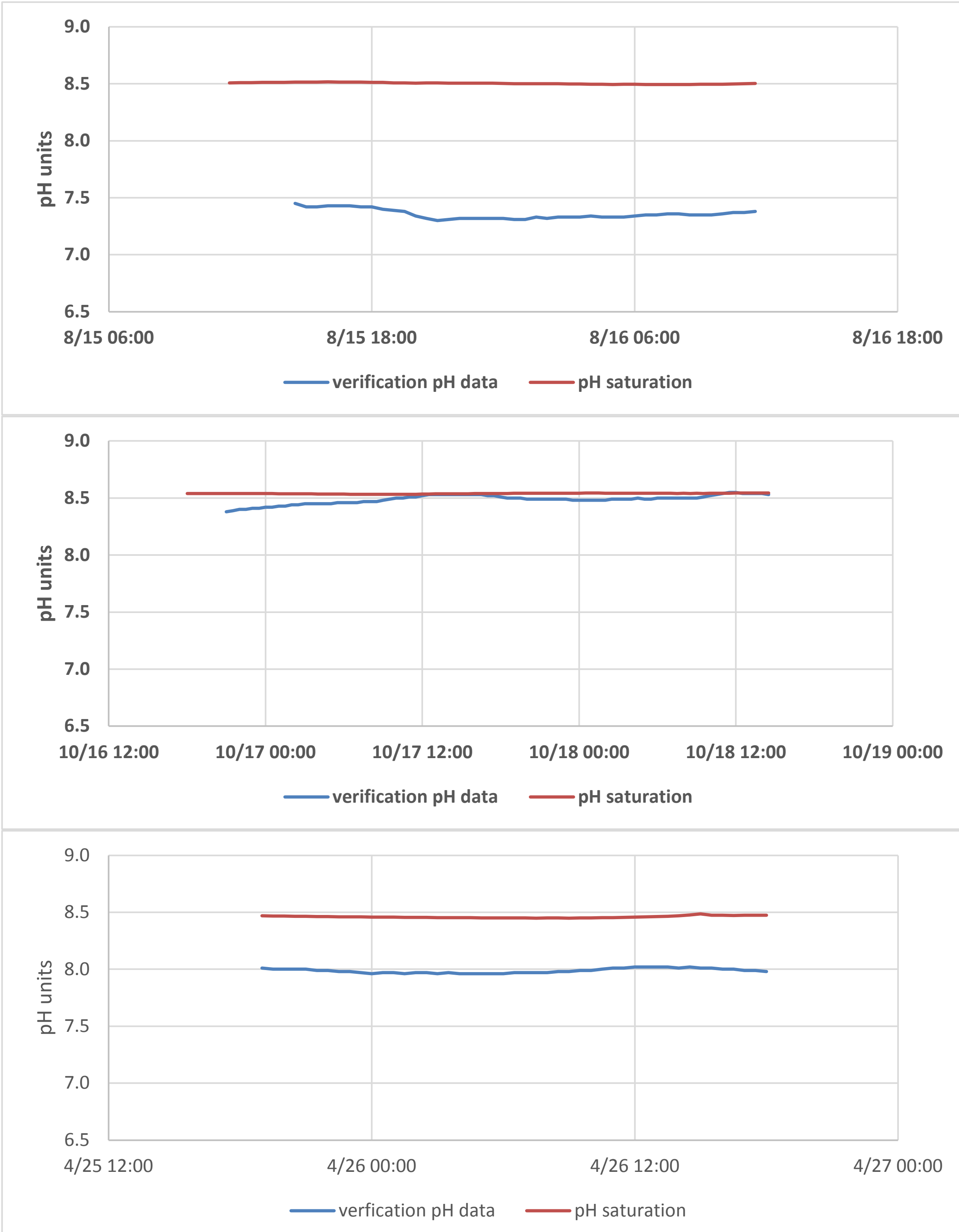


Figure 14. Results of pH time series for Tunk Creek verification monitoring in August and October 2015 and April 2016.

Comparison of the October pH verification data in Tunk Creek to pH saturation levels shows that the pH in the creek was essentially at or near the saturation levels (Figure 14).

Based on the diel amplitude differences being less than 0.10 pH units (Table 9), this study is satisfied that the pH exceedance in Tunk Creek is due to the pH levels being at equilibrium with or near to natural saturation conditions and not caused by anthropogenic influences. Accordingly, this study recommends delisting Tunk Creek from the 303(d) list for pH.

Chiliwist Creek

Chiliwist Creek has only a lower reach on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. Most of the pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

Verification pH monitoring on lower Chiliwist Creek showed values above the upper criterion of 8.5 pH units in August 2015 and April 2016 with diel range generally between 8.46 and 8.62 pH units (Figure 15).

Chiliwist Creek was diluted by low ionic water during the August 2015 monitoring period, with corresponding dip in estimated saturated pH levels. The observed pH levels remained relatively constant except for decrease when a slug of higher ionic water passed in the middle of the day. The source of the low ionic water is unknown; there was no rainfall during the survey (Figure 15).

The October 2015 pH levels in Chiliwist Creek were between 8.08 and 8.12 pH units. Comparison of the April 2016 pH verification data to pH saturation levels shows that the pH in the creek was essentially at or near the saturation level for the monitoring period (Figure 15).

Based on the diel amplitude differences being less than 0.10 pH units (Table 9), this study is satisfied that the pH exceedances in Chiliwist Creek is due to the pH levels being at equilibrium with or near to natural saturation conditions and not caused by anthropogenic influences. Accordingly, this study recommends delisting Chiliwist Creek from the 303(d) list for pH.

Sinlahekin Creek

An upper reach on Sinlahekin Creek is on the 303(d) list for pH. The basis for the pH listing is monitoring data collected by the Okanogan CD from 2000-2003. The pH exceedances were from the early monitoring (summer 2000-01) when all the pH data appears to have been biased high.

Sinlahekin Creek runs through a series of lakes (Forde and Connors) through the Sinlahekin Valley before running into Palmer Lake. The upper 303(d)-listed site for pH is directly below the outlet of Connors Lake. The water quality of Connors Lake directly influences this site. Forde and Connors lakes appeared productive in April 2016, with a green-colored tint from an apparent spring algae bloom.

The pH verification monitoring in Sinlahekin Creek was moved to a location about 2 miles downstream of Connors Lake outlet (at the Cecile Creek Rd crossing) to capture the water quality dynamics of the creek and not the lake. Ecology has maintained a streamflow gage site at this location, although it is no longer managed.

The pH verification monitoring showed a classic response of algal productivity in the August 2015 and October 2015 pH data, with the diel fluctuation increasing in the afternoon and decreasing at night (Figure 16). The diel fluctuation signal was weaker in October but still recognizable with pH levels above the criteria and saturation for part of the day.

Diel amplitude differences were greater than 0.10 pH units in August and October 2015 (Table 9). During the verification monitoring Ecology noted macrophytes and filamentous algae in the sunlit water column in both August and October 2015.

In April 2016 there was high spring runoff and the water was very turbid, creating a light limitation for productivity. The pH varied only 0.1 pH units throughout the day, from 7.87 to 7.97 pH units.

Nutrient concentrations were measured by the Okanogan CD monthly from spring of 2000 to the spring of 2003. Nutrient levels were influenced by Connors Lake dynamics but showed nitrogen limitation throughout the monitoring project with most growing months having levels below the reporting limit of 0.01 mg/L. Ortho-phosphate concentrations were relatively steady between 0.01 and 0.03 mg/L throughout the monitoring, with the lowest levels, below the reporting limit of 0.01 mg/L, appearing in April and May, probably due to spring blooms in the lake.

Aerial photography shows that the riparian does not cover or shade the creek very much between Connors Lake and Cecile Creek Rd, so light limitation of productivity from shading is very limited, which may or may not be natural. The Sinlahekin Valley has been heavily managed for timber and grazing for over a century.

Ecology cannot determine from the data how much of the biological activity in Sinlahekin Creek is due to natural or anthropogenic causes; therefore, this study recommends keeping the creek on the 303(d) list for pH impairment.

Summary of recommendations for verification monitoring showing exceedances of pH criteria

In summary, this study recommends delisting verification sites on Siwash, Johnson, Tunk, and Chiliwist Creeks which are on the 2012 303(d) list for pH. In addition, other listed reaches on Siwash, Johnson, and Tunk Creeks that were not re-monitored during the verification study are also recommended to be delisted because the verification study used the monitored sites as proxies for the verification of all other reaches on the same tributaries. Table 10 summarizes the listings recommended for delisting.

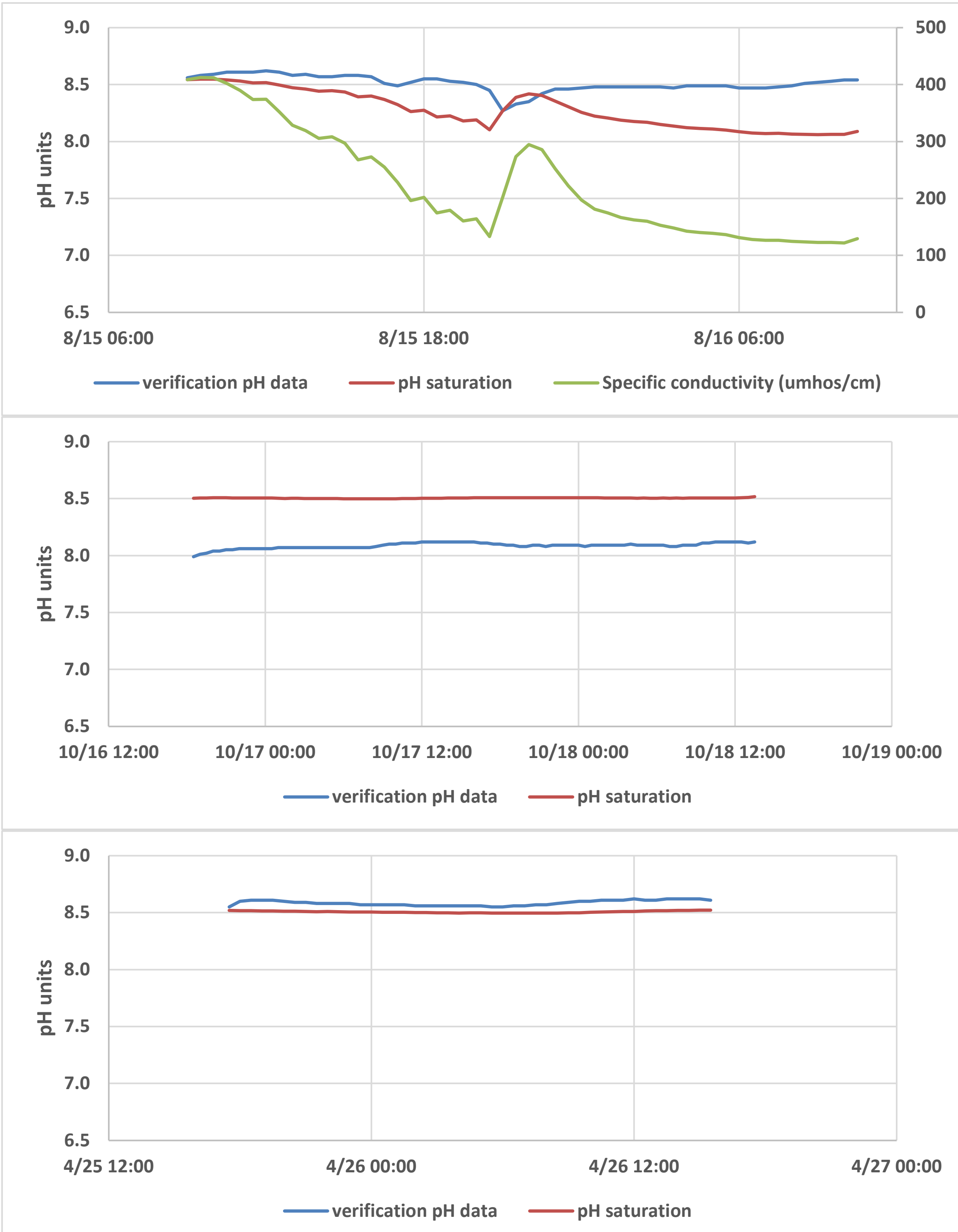


Figure 15. Results of pH time series for Chiliwist Creek verification monitoring in August and October 2015 and April 2016.

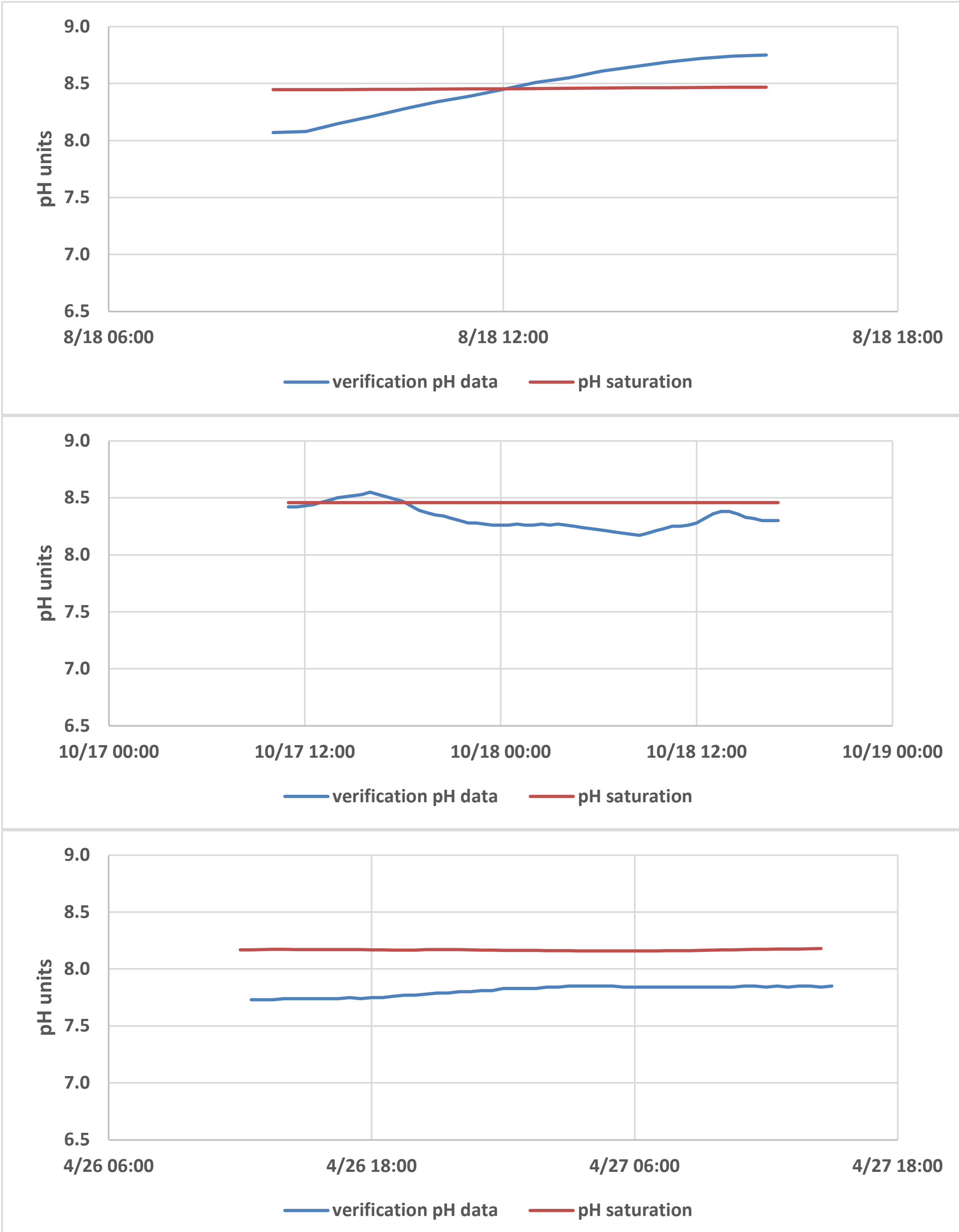


Figure 16. Results of pH time series for Sinlahekin Creek verification monitoring in August and October 2015 and April 2016.

Table 10. Okanogan River tributary segments with pH listing on the 2012 303(d) list with a recommendation to delist for pH.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Siwash Creek	41289	1194384487121	0.77	0.07
Siwash Creek	50591	1194384487121	13.88	12.07
Johnson Creek	41288	1195057485045	1.06	0.00
Johnson Creek	50604	1195057485045	12.21	11.21
Tunk Creek	41830	1194868485618	2.91	0.58
Tunk Creek	50602	1194868485618	13.58	11.63
Chiliwist Creek	41286	1197369482463	2.55	0.48

In addition, there is a new Tunk Creek listing for pH on the current 2014 303(d) list, recently approved by EPA. The new listing is for a segment reach just downstream and adjacent to the lower 2012 listing reach. This new listing was incorporated into the 2012 listing #41830 which now extends to the mouth of the creek.

Table 11 shows the new pH listing for Tunk Creek on the current 303(d) list. This verification study monitored a site very close to the new listing reach. This evaluation recommends using the same decision-making criteria that was used for other un-verified reaches. Specifically, the monitored site used in the verification study will be a proxy for the verification of all other listed reaches on the same tributary.

Table 11. Tunk Creek segment with pH listing on the current 303(d) list recommended for delisting.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Tunk Creek	41830	1194868485618	2.91	0.00

This study could not determine from the verification data how much of the biological activity in Sinlahekin Creek was due to natural or anthropogenic causes; therefore, this study recommends keeping the creek on the 303(d) list for pH impairment (Table 12).

Table 12. Sinlahekin Creek segment with pH listing on the current 303(d) list that this 2015-2016 study recommends to keep on the list for potential pH impairment.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Sinlahekin Creek	51200	1196463487988	19.30	17.20

Discussion

Eighteen of 19 reaches on Okanogan River tributaries which are listed on the 303(d) list for pH impairment were found to not have exceedances of the pH standards in this verification study.

The basis for the 303(d) listings was biased pH data collected by the Okanogan CD in 2000-2003 and submitted to Ecology's EIM database.

Nevertheless, verification monitoring did show that Okanogan River tributaries have a tendency to have high pH levels, with some exceeding the upper pH criterion of 8.5 pH units. Even in cases where monitoring showed levels meeting pH criteria, the levels were sometimes just below the upper criterion of 8.5 pH units.

High alkalinity in the tributaries is a result of natural carbonate geology in the Okanogan basin. High alkalinity also results in higher pH saturation in the Okanogan River tributaries, often higher than the pH criteria.

A pH model was used in this verification study to determine pH saturation levels. The model showed that any tributary with alkalinity over 125 mg/L as $CaCO_3$ will have saturation pH levels over the pH criteria. Most of the basin tributaries have alkalinities over 125 mg/L.

Comparing pH saturation to observed pH levels is a good analysis to see if biological activity is affecting pH levels. In most cases the verification monitoring found that pH matched or closely paralleled the saturation potential throughout the day, showing the pH levels in the tributaries were in an equilibrium state with the pH saturation potential.

In cases where the tributary pH was below saturation but mimicked the saturation time concentration curve, the source water to the stream was probably not at saturation when it entered the stream. Most of the Okanogan River tributaries are principally groundwater-fed for part of the year, and groundwater inflows are usually low in pH (oversaturated with carbon dioxide) and not in equilibrium with atmospheric carbon dioxide. Carbonate ions leaching out of the geologic formations enrich the carbonate system in the water decreasing the pH below saturation.

Biological processes were found to only affect the upper Sinlahekin Creek which had diel fluctuations above and below saturation levels. Sinlahekin Creek is also on the 303(d) list for dissolved oxygen and water temperature impairment. This study was not designed to separate natural productivity from productivity induced by nutrient enrichment or other anthropogenic activities.

In general, most of the tributaries that Ecology monitored for the verification study were very small in size and well-vegetated with a dense riparian canopy and undercover. There was enough shade to limit productivity, with the exception of larger tributaries like Loup Loup Creek which had moderate cover and Sinlahekin Creek, which had sparse cover.

Conclusions

Results of this 2015-2016 study support the following conclusions.

- A comparison of the observed pH data collected by the Okanogan Conservation District (CD) in 2000-2003 to pH saturation levels supports the premise that the Okanogan CD pH data has a uniform bias, most likely caused by a failing pH sensor. The early period of monitoring, especially from summer of 2000 to summer of 2001, appears to be biased high which may have led to erroneous listings in most tributaries within the basin. Later periods appear to be biased low. No quality assurance data are available to validate the monitoring data.

- This conclusion corroborates the data quality assessment made earlier that found no correlation between the measured pH by the Okanogan CD and other factors (seasonality, time of day, stream temperature, or streamflow) to explain the meandering bias shifts in pH throughout the 3-year monitoring period.

- Ecology collected diel pH data in 11 tributaries during the summer and fall of 2015 and spring of 2016 to verify the pH impairment listings. The verification pH measurements ranged from 7.15 to 8.75 throughout the basin for all three monitoring periods.

- With the exception of Sinlahekin Creek, most diel measurements exhibited mostly flat-lined pH signals over the course of the day, indicating very little productivity in the water.

- Verification monitoring with measurements over the upper pH criterion of 8.5 pH units were compared to calculated pH saturation. The calculated pH saturation for many of the streams in the Okanogan River basin was very near and sometimes higher than the upper pH criterion of 8.5 pH units. This was due to the naturally high alkalinity in the water from basin geo-chemical sources. Carbonate ions leaching out of the geologic formations enrich the carbonate system in the water, decreasing the pH below saturation.

- In most cases, the comparison of the pH measurements over 8.5 and the calculated pH saturation showed that the pH in the tributary was at or approaching saturation, in natural equilibrium with the chemical composition of the water.

- Verification monitoring in Bonaparte Creek, conducted "in situ", showed that the pH in the creek was usually just below saturation, while the pH saturation was usually above the 8.5 criterion. The pH levels in the creek were at an equilibrium pH straddling just below the 8.5 upper criterion. Ecology's Freshwater Monitoring Unit (FMU) collected monthly measurements of pH from Bonaparte Creek in 2014 and 2015 with many measurements above the 8.5 pH criterion, but likely introduced a bias with their sampling methodology by taking a sample of water out of the creek and letting it equilibrate to the atmosphere in a sample cup before measurement.

- The streamflow in all tributaries were at baseflow for the August and October 2015 verification monitoring. High conductivities suggest groundwater inflow as the source of baseflow to the streams. Even though there was a drought in 2015, low flows appear common to most years. Bankfull widths in many streams were so narrow a person could jump over them. The arid landscape in many of the tributaries does not produce very much streamflow.

- Only Loup Loup and Sinlahekin Creeks, with watersheds extending into the higher elevations of the Cascades on the west side of the Okanogan River, produced large spring runoff conditions (at least 100 cfs) during the verification monitoring in April 2016. East-side tributaries, Bonaparte and Tunk, had much smaller but moderate spring runoff. The rest of the tributaries barely had April streamflow higher than their summer and fall flow.

- Most of the tributaries were well shaded, with dense riparian areas where left undisturbed. The shade (light limitation) probably contributes to a relative lack of productivity in the streams. Nutrient data collected by the Okanogan CD in 2000-2003 also showed a lack of nitrogen as a potential limitation at some sites during the growing season.

- Minimal productivity meant that the pH in most streams was near saturation. Even if the pH was not at saturation, the diel sampling showed minimal amplitudes, paralleling the pH saturation time concentration curve. Some sites, like Tunk Creek, had pH levels below saturation during baseflow, probably indicating that groundwater inflow was lower in pH and reaeration insufficient to equilibrate to saturation levels at the sampling location.

- There are dissolved oxygen (DO) listings for some Okanogan River tributaries based on the Okanogan CD data collected in 2000-2003 (see Appendix F). Like the pH data, the DO data has no quality assurance records and should be qualified in EIM database as not suitable for assessment of DO conditions.

- Sinlahekin Creek shows signs of biological productivity and it is not clear if this is due to natural or anthropogenic causes, so both DO listings on Sinlahekin Creek should remain on the 303(d) list for further investigation.

- DO listings were evaluated for the other tributaries (Appendix F) based on the biological activity measured during the verification study. This study shows that there was de minimis biological activity in the creeks and, therefore, anthropogenic causes were unlikely to cause exceedances of DO criteria. Accordingly, Ninemile, Tonasket, and Loup Loup Creeks should be removed from the 303(d) list for DO impairment.

Recommendations

Results of this 2015-2016 study support the following recommendations.

1. The pH data collected by the Okanogan CD does not have existing quality assurance documentation. All of the data appear to be biased and should be rejected or at least qualified in EIM (Study ID #G0000225). This also applies to their dissolved oxygen (DO) data. The *Study QA Assessment Level* status for the grant project in EIM is currently set to high quality, verified data (Level 4). The status should be changed to unverified data (Level 1).

2. Ecology needs more stringent evaluation of the data collected by grantees. There needs to be audits of the data collection methods and quality assurance/quality control (QA/QC) protocols and assessments. Documentation of all QA/QC data should be available in a data summary or final report that includes a final QA assessment to determine if the measurement quality objectives (MQO) were met. No data should be submitted to EIM that has not been quality assured to meet the project MQOs and properly qualified. Steps that could assist in better collection of data by grantees include:

    - Training workshops for grant recipients on proper calibration methods, QA assessment methods, and QA/QC documentation.
    - Better Standard Operating Procedure (SOP) documentation that clearly spells out the QA/QC procedures and required QA/QC documentation (maybe include forms) that recipients must follow in order to have their data approved.
    - Audits in the field by Ecology staff with side-by-side comparison of field measurements.
    - Review of data QA assessment and qualified data before it is uploaded to EIM by grant recipient (maybe include a formal approval step here from Ecology before EIM uploading)
    - Review of draft data summary reports and final reports (making sure QA/QC data assessment is documented in reports). Some grant recipients could also use some guidance on how to present data in their reports.

3. This technical analysis shows with a high level of certainty that pH exceedances in some basins are of natural origin due to the geochemistry within the basin. Some basins in eastern Washington have naturally high alkalinity in their water, where the natural pH saturation levels will be above the current pH criteria. Ecology should consider extending the upper pH criterion from 8.5 to 9.0 pH units in some eastern Washington basins or provide for some level of allowable increase above natural pH when the natural pH is above 8.5.

    - Ecology should re-evaluate the pH standards in a similar way to how the State of Oregon did for their pH standard (DEQ, 1995). As shown by this current verification study, there are some streams that have high alkalinity that result in an equilibrium pH above the upper 8.5 pH criterion.
    - Using another Oregon example, a pH exceedance of a given magnitude could serve as an action limit to protect beneficial uses which would trigger a study designed to determine

the cause of the exceedance. For example, a pH of over 8.7 where the criterion is 9.0 could automatically result in the initiation of a synoptic study (including diel sampling for pH, temperature, DO, and nutrients) to determine if there are anthropogenic causes for the elevated pH.

- An alkalinity threshold of 150 mg/L (with a margin of safety) could be used to designate which streams the extension to an upper 9.0 pH criterion is applied.

4. Ecology's Freshwater Monitoring Unit (FMU) should re-design their monitoring program to measure pH and DO in the stream and not on a sample taken out of the stream.
   - FMU should sample any stream with conductivities over 200 umhos/cm for alkalinity so that the saturated pH can be calculated for that sample day.

5. The following tributary reaches should be delisted for pH from the current 303(d) list for pH impairment.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Tonasket Creek	41831	1194229489371	1.64	0.00
Tonasket Creek	50595	1194229489371	8.90	7.34
Antoine Creek	41827	1194112487614	0.77	0.00
Ninemile Creek	41326	1194333489670	2.18	0.52
Ninemile Creek	51195	1194333489670	10.92	9.52
Tallant Creek	50616	1196594482977	10.06	7.90
Tallant Creek	50615	1196594482977	1.46	0.00
Loup Loup Creek	41828	1197043482804	1.67	0.00
Bonaparte Creek	41280	1194456487053	1.18	0.00
Bonaparte Creek	50599	1194456487053	4.095	2.026
Bonaparte Creek	50600	1194456487053	24.66	22.11
Siwash Creek	41289	1194384487121	0.77	0.07
Siwash Creek	50591	1194384487121	13.88	12.07
Johnson Creek	41288	1195057485045	1.06	0.00
Johnson Creek	50604	1195057485045	12.21	11.21
Tunk Creek	41830	1194868485618	2.91	0.00
Tunk Creek	50602	1194868485618	13.58	11.63
Chiliwist Creek	41286	1197369482463	2.55	0.48

6. The following tributary reach should remain listed for pH on the 303(d) list for pH impairment:

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Sinlahekin Creek	51200	1196463487988	19.30	17.20

7. The following tributary reaches were verified to not have DO exceedances and should be delisted for DO impairment on the 303(d) list:

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Ninemile Creek	47926	1194333489670	2.18	0.52
Ninemile Creek	47927	1194333489670	10.92	9.52

8. The following tributary reaches were not verified directly but should be removed from the 303(d) list for DO impairment because lower reaches on the creeks show de minimis biological activity and no exceedances of pH standards.

Waterbody Name	Listing ID	LLID Number	LLID upper	LLID lower
Tonasket Creek	47284	1194229489371	8.90	7.34
Loup Loup Creek	47933	1197043482804	18.68	16.88

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Appendices

Appendix A. Quality assurance assessment

QA of the verification monitoring data.

The measurement quality objectives (MQOs) for pH measurements for the study were established in the study QA Project Plan (Carroll, 2015) and are listed in Table A-1.

Table A-1. Measurement quality objectives for Hydrolab post-deployment pH bias checks.

Parameter	Units	Accept	Qualify	Reject
pH	std. units	< or = $\pm$ 0.2	> $\pm$ 0.2 and < or = $\pm$ 0.8	> $\pm$ 0.8

The pH sensors on all of the Hydrolab dataloggers used in the study had acceptable pre-calibration checks (Table A-2) and post-calibration checks based on the MQOs established for the study (Table A-3).

Table A-2. Results of the pre-calibration of pH sensors. The Sonde number is an Ecology designation for a specific Hydrolab multi-parameter sonde datalogger.

			pH 7 Standard				pH 9 Standard			
Field Use Date/s	Pre-Cal Date	Sonde #	(temp corrected) Reference standard value	Hydrolab check value (before calibration)	Hydrolab check value (after calibration)	Temp	(temp corrected) Reference standard value	Hydrolab check value (before calibration)	Hydrolab check value (after calibration)	Temp
August 14-19, 2015	8/14/2015	26	7.00	7.00	10.00	NA	10.00	10.00	10.00	NA
August 14-19, 2015	8/14/2015	31	7.00	7.06	7.00	22.50	10.00	9.93	10.00	22.44
August 14-19, 2015	8/14/2015	33	7.01	7.06	7.01	25.17	10.03	9.96	10.03	22.28
August 14-19, 2015	8/14/2015	34	7.01	7.22	7.00	22.29	10.03	9.90	10.04	22.39
August 14-19, 2015	8/14/2015	37	7.00	6.95	7.00	22.72	10.00	10.01	10.00	22.00
August 14-19, 2015	8/14/2015	39	7.00	7.12	7.00	22.50	10.00	9.97	10.00	22.50
August 14-19, 2015	8/13/2015	52	7.01	NA	7.05	22.56	10.03	NA	10.03	22.38
August 14-19, 2015	8/14/2015	53	7.01	6.91	7.01	22.24	10.03	9.97	10.03	22.46
August 14-19, 2015	8/14/2015	54	7.00	6.89	7.01	22.20	10.00	9.97	10.00	22.40
August 14-19, 2015	8/14/2015	55	7.01	6.98	7.01	22.28	10.03	9.99	10.03	22.42
October 15-21, 2015	10/15/2015	15	7.01	7.07	7.00	21.87	10.04	10.02	10.04	21.52
October 15-21, 2015	10/15/2015	18	7.02	7.09	7.02	20.80	10.04	10.05	10.04	20.70
October 15-21, 2015	10/15/2015	31	7.02	7.22	7.01	21.37	10.05	10.01	10.05	21.11
October 15-21, 2015	10/15/2015	40	7.01	7.31	7.02	21.50	10.03	9.97	10.03	21.40
October 15-21, 2015	10/15/2015	43	7.01	7.07	7.01	21.80	10.04	9.87	10.04	21.60
October 15-21, 2015	10/15/2015	44	7.00	7.00	6.99	21.50	10.04	9.94	10.05	21.60
October 15-21, 2015	10/15/2015	45	7.02	6.99	7.02	21.72	10.05	10.03	10.05	21.30
October 15-21, 2015	10/15/2015	52	7.02	7.14	7.02	21.18	10.05	10.04	10.05	21.04
October 15-21, 2015	10/15/2015	53	7.00	7.09	7.00	21.22	10.00	10.10	10.00	21.00
October 15-21, 2015	10/15/2015	54	7.01	7.05	7.01	22.40	10.03	10.05	10.02	21.80
October 15-21, 2015	10/15/2015	55	7.00	7.19	7.00	21.45	10.00	10.14	10.00	21.40
April 25-28, 2016	4/26/2016	25	7.06	6.81	7.01	11.34	10.16	10.07	10.00	11.34
April 25-28, 2016	4/26/2016	41	7.06	6.98	7.05	10.95	10.15	9.84	9.92	11.60
April 25-28, 2016	4/25/2016	45	7.00	7.00	7.00	20.26	10.00	9.96	10.01	20.43
April 25-28, 2016	4/25/2016	52	7.00	7.02	7.00	20.28	10.00	9.85	10.00	19.95
April 25-28, 2016	4/25/2016	53	7.00	6.94	6.99	19.67	10.00	10.01	10.00	19.30
April 25-28, 2016	4/25/2016	54	7.00	6.96	7.00	19.95	10.00	10.04	10.00	19.24
April 25-28, 2016	4/25/2016	55	7.00	6.98	7.00	20.08	10.00	10.07	10.00	20.20

Table A-3. Results of the post-calibration of pH sensors. The Sonde number is an Ecology designation for a specific Hydrolab multi-parameter datalogger.

			pH 7 Standard					pH 9 Standard				
Field Use Date/s	Post-Check Date	Sonde #	(temp corrected) Reference standard value	Hydrolab post-check value (before calibration)	Difference	Temp	Conclusion	(temp corrected) Reference standard value	Hydrolab post-check value (before calibration)	Difference	Temp	Conclusion
August 14-19, 2015	8/19/2015	26	7.00	7.00	0.00	72.40	accept	10.00	9.98	-0.02	72.5	accept
August 14-19, 2015	8/19/2015	31	7.00	6.97	-0.03	22.40	accept	10.00	10.09	0.09	22.49	accept
August 14-19, 2015	8/19/2015	33	7.00	6.97	-0.03	22.30	accept	10.00	10.01	0.01	22.41	accept
August 14-19, 2015	8/19/2015	34	7.00	7.06	0.06	72.00	accept	10.00	10.03	0.03	72.3	accept
August 14-19, 2015	8/19/2015	37	7.00	7.01	0.01	72.40	accept	10.00	10	0.00	72.5	accept
August 14-19, 2015	8/19/2015	39	7.00	7.06	0.06	72.20	accept	10.00	10.02	0.02	72.2	accept
August 14-19, 2015	8/19/2015	52	7.00	7.17	0.17	72.20	accept	10.00	10.13	0.13	72.2	accept
August 14-19, 2015	8/19/2015	53	7.02	7.06	0.04	20.86	accept	10.03	10.08	0.05	22.03	accept
August 14-19, 2015	8/19/2015	54	7.01	6.96	-0.05	22.32	accept	10.03	9.98	-0.05	22.31	accept
August 14-19, 2015	8/19/2015	55	7.01	6.90	-0.11	22.34	accept	10.03	9.92	-0.11	22.43	accept
October 15-21, 2015	10/21/2015	15	7.04	7.01	-0.03	20.30	accept	10.05	10.04	-0.01	20.3	accept
October 15-21, 2015	10/19/2015	18	7.01	7.00	-0.01	21.30	accept	10.04	10.01	-0.03	20.14	accept
October 15-21, 2015	10/19/2015	31	7.01	7.04	0.03	22.00	accept	10.04	10.06	0.02	21.4	accept
October 15-21, 2015	10/19/2015	40	7.01	7.09	0.08	21.65	accept	10.04	10.04	0.00	21.33	accept
October 15-21, 2015	10/19/2015	43	7.01	7.00	-0.01	21.19	accept	10.04	10.05	0.01	21.29	accept
October 15-21, 2015	10/20/2015	44	7.01	7.00	-0.01	21.88	accept	10.04	10.05	0.01	21.5	accept
October 15-21, 2015	10/20/2015	45	7.01	7.02	0.01	22.06	accept	10.04	10.03	-0.01	21.57	accept
October 15-21, 2015	10/19/2015	52	7.01	7.08	0.07	21.90	accept	10.04	10.05	0.01	21.4	accept
October 15-21, 2015	10/19/2015	53	7.01	7.00	-0.01	21.40	accept	10.04	10.02	-0.02	21.08	accept
October 15-21, 2015	10/19/2015	54	7.01	7.01	0.00	21.70	accept	10.04	10.07	0.03	21.19	accept
October 15-21, 2015	10/19/2015	55	7.01	6.91	-0.10	21.60	accept	10.04	9.99	-0.05	21.2	accept
April 25-28, 2016	4/28/2016	25	7.02	7.12	0.10	20.20	accept	10.05	10.14	0.09	19.49	accept
April 25-28, 2016	4/28/2016	41	7.02	7.08	0.06	20.16	accept	10.05	10.1	0.05	19.49	accept
April 25-28, 2016	4/28/2016	45	7.02	7.02	0.00	20.00	accept	10.05	9.98	-0.07	19.66	accept
April 25-28, 2016	4/28/2016	52	7.02	7.09	0.07	20.08	accept	10.05	10.08	0.03	19.52	accept
April 25-28, 2016	4/28/2016	53	7.02	7.09	0.07	19.18	accept	10.05	10.1	0.05	19.15	accept
April 25-28, 2016	4/28/2016	54	7.02	7.01	-0.01	19.79	accept	10.05	10.04	-0.01	19.24	accept
April 25-28, 2016	4/28/2016	55	7.02	7.03	0.01	19.85	accept	10.05	10.02	-0.03	19.33	accept

In addition, specific conductivity was measured during the study. The MQOs for conductivity measurements common for the studies of this kind are listed in Table A-4.

Table A-4. Measurement quality objectives for Hydrolab post-deployment conductivity bias checks.

Parameter	Units	Accept	Qualify	Reject
Specific conductivity	umhos/cm	< or = ± 5%	> ± 5% and < or = ± 15%	> ± 15%

The conductivity sensors on all of the Hydrolab dataloggers used in the study had acceptable pre-calibration checks (Table A-5) and post-calibration checks based on the MQOs established for the study (Table A-6).

Table A-5. Results of the pre-calibration of conductivity sensors. The Sonde number is an Ecology designation for a specific Hydrolab multi-parameter sonde datalogger.

			Conductivity 100µS Standard				Conductivity 1000µS Standard			
Field Use Date/s	Pre-Cal Date	Sonde #	Reference standard value	Hydrolab check value (before calibration)	Hydrolab check value (after calibration)	Temp	Reference standard value	Hydrolab check value (before calibration)	Hydrolab check value (after calibration)	Temp
August 14-19, 2015	8/14/2015	26	100.0	100.0	100.0	NA	NA	NA	NA	NA
August 14-19, 2015	8/14/2015	31	0.0	NA	0.0	NA	1000.0	1323.0	999.0	22.56
August 14-19, 2015	8/14/2015	33	100.0	NA	101.0	22.61	1000.0	1004.0	NA	22.67
August 14-19, 2015	8/14/2015	34	100.0	NA	101.0	22.50	1000.0	996.7	1000.0	22.28
August 14-19, 2015	8/14/2015	37	NA	NA	NA	NA	NA	NA	NA	NA
August 14-19, 2015	8/14/2015	39	0.0	NA	0.0	NA	1000.0	1000.0	1000.0	22.60
August 14-19, 2015	8/13/2015	52	100.0	NA	100.4	22.30	1000.0	NA	1004.0	22.20
August 14-19, 2015	8/14/2015	53	100.0	NA	97.7	22.62	1000.0	988.1	1000.0	22.49
August 14-19, 2015	8/14/2015	54	0.0	NA	0.0	NA	1000.0	995.8	1000.0	22.40
August 14-19, 2015	8/14/2015	55	100.0	NA	97.0	22.53	1000.0	1001.3	1000.0	20.33
October 15-21, 2015	10/15/2015	15	100.0	NA	104.2	22.02	1000.0	1035.0	1001.0	21.83
October 15-21, 2015	10/15/2015	18	100.0	NA	98.1	21.20	1000.0	999.3	1000.0	20.80
October 15-21, 2015	10/15/2015	31	100.0	NA	101.5	21.92	1000.0	995.1	1002.0	21.82
October 15-21, 2015	10/15/2015	40	100.0	NA	112.0	21.80	1000.0	1002.0	1000.0	21.50
October 15-21, 2015	10/15/2015	43	100.0	NA	111.8	22.10	1000.0	997.5	1000.0	21.90
October 15-21, 2015	10/15/2015	44	100.0	NA	99.7	22.10	1000.0	995.8	1000.0	21.90
October 15-21, 2015	10/15/2015	45	100.0	NA	102.1	22.03	1000.0	1016.0	999.6	21.99
October 15-21, 2015	10/15/2015	52	100.0	NA	99.5	21.74	1000.0	993.3	1000.0	21.66
October 15-21, 2015	10/15/2015	53	100.0	NA	108.6	21.40	1000.0	1008.0	NA	21.40
October 15-21, 2015	10/15/2015	54	100.0	NA	108.3	22.20	1000.0	1008.0	1000.0	22.10
October 15-21, 2015	10/15/2015	55	100.0	NA	107.7	21.40	1000.0	1004.6	1000.0	21.20
April 25-28, 2016	4/26/2016	25	100.0	100.2	100.0	20.51	1000.0	1013.0	999.9	20.17
April 25-28, 2016	4/26/2016	41	100.0	100.8	99.4	20.39	1000.0	966.3	999.6	20.44
April 25-28, 2016	4/25/2016	45	100.0	101.5	99.9	20.75	1000.0	989.1	999.7	20.43
April 25-28, 2016	4/25/2016	52	0.0	0.0	0.0	NA	1000.0	1005.0	1000.0	20.19
April 25-28, 2016	4/25/2016	53	100.0	99.9	99.9	20.00	1000.0	1004.8	1000.0	20.00
April 25-28, 2016	4/25/2016	54	100.0	100.4	100.1	20.15	1000.0	1000.4	1000.0	20.20
April 25-28, 2016	4/25/2016	55	100.0	98.0	100.0	20.36	1000.0	1015.0	999.4	20.34

Table A-6. Results of the post-calibration of conductivity sensors. The Sonde number is an Ecology designation for a specific Hydrolab multi-parameter datalogger.

			Conductivity 100µS Standard					Conductivity 1000µS Standard				
Field Use Date/s	Post-Check Date	Sonde #	Reference standard value	Hydrolab check value (before calibration)	Difference	Temp	Conclusion	Reference standard value	Hydrolab check value (before calibration)	Difference	Temp	Conclusion
August 14-19, 2015	8/19/2015	26	100	101	1.00%	22.78	accept	1000	1006	0.60%	22.61	accept
August 14-19, 2015	8/19/2015	31	100	99	-1.00%	22.39	accept	1000	1006	0.60%	22.33	accept
August 14-19, 2015	8/19/2015	33	100	99.9	-0.10%	22.61	accept	1000	1008	0.80%	22.62	accept
August 14-19, 2015	8/19/2015	34	100	98	-2.00%	22.56	accept	1000	1007	0.70%	22.44	accept
August 14-19, 2015	8/19/2015	37	100	99	-1.00%	22.94	accept	1000	1011	1.10%	22.67	accept
August 14-19, 2015	8/19/2015	39	100	102	2.00%	22.44	accept	1000	1007	0.70%	22.44	accept
August 14-19, 2015	8/19/2015	52	100	100	0.00%	22.61	accept	1000	1006	0.60%	22.56	accept
August 14-19, 2015	8/19/2015	53	100	99.9	-0.10%	21.22	accept	1000	1001.7	0.17%	22.50	accept
August 14-19, 2015	8/19/2015	54	100	98.3	-1.70%	22.46	accept	1000	1002.8	0.28%	22.59	accept
August 14-19, 2015	8/19/2015	55	100	96.6	-3.40%	22.64	accept	1000	994.5	-0.55%	22.46	accept
October 15-21, 2015	10/21/2015	15	100	104.2	4.20%	20.90	accept	1000	1001	0.10%	20.80	accept
October 15-21, 2015	10/19/2015	18	100	97.2	-2.80%	21.75	accept	1000	991.6	-0.84%	21.65	accept
October 15-21, 2015	10/19/2015	31	100	103.9	3.90%	22.00	accept	1000	997.2	-0.28%	22.00	accept
October 15-21, 2015	10/19/2015	40	100	99.7	-0.30%	21.90	accept	1000	996.7	-0.33%	21.85	accept
October 15-21, 2015	10/19/2015	43	100	104.9	4.90%	21.94	accept	1000	996.1	-0.39%	21.75	accept
October 15-21, 2015	10/20/2015	44	100	101.3	1.30%	22.00	accept	1000	998.7	-0.13%	21.90	accept
October 15-21, 2015	10/20/2015	45	100	100.2	0.20%	22.18	accept	1000	1000	0.00%	21.92	accept
October 15-21, 2015	10/19/2015	52	100	101.9	1.90%	22.10	accept	1000	999	-0.10%	22.00	accept
October 15-21, 2015	10/19/2015	53	100	100.6	0.60%	21.80	accept	1000	998	-0.20%	21.80	accept
October 15-21, 2015	10/19/2015	54	100	102.7	2.70%	21.98	accept	1000	998.6	-0.14%	21.77	accept
October 15-21, 2015	10/19/2015	55	100	99.2	-0.80%	22.00	accept	1000	997.1	-0.29%	21.90	accept
April 25-28, 2016	4/28/2016	25	100	100.6	0.60%	20.33	accept	1000	1002	0.20%	20.20	accept
April 25-28, 2016	4/28/2016	41	100	100.4	0.40%	20.28	accept	1000	1002	0.20%	20.19	accept
April 25-28, 2016	4/28/2016	45	100	100.5	0.50%	20.33	accept	1000	999.7	-0.03%	20.32	accept
April 25-28, 2016	4/28/2016	52	100	101.4	1.40%	20.39	accept	1000	997.1	-0.29%	20.33	accept
April 25-28, 2016	4/28/2016	53	100	100.6	0.60%	19.95	accept	1000	1004.6	0.46%	19.83	accept
April 25-28, 2016	4/28/2016	54	100	99.8	-0.20%	20.23	accept	1000	998.2	-0.18%	20.18	accept
April 25-28, 2016	4/28/2016	55	100	99.7	-0.30%	20.16	accept	1000	998.1	-0.19%	20.16	accept

In addition, dissolved oxygen was measured at a couple of tributary sites. The data is presented in Appendix F. The MQOs for dissolved oxygen measurements common for the studies of this kind are listed in Table A-7.

Table A-7. Measurement quality objectives for Hydrolab post-deployment dissolved oxygen percent saturation bias checks.

Parameter	Units	Accept	Qualify	Reject
Dissolved Oxygen saturation	%	< or = ± 5%	> ± 5% and < or = ± 15%	> ± 15%

The dissolved oxygen sensors on all of the Hydrolab dataloggers used in the study had acceptable pre- and post-calibration checks (Table A-8) based on the MQOs.

Table A-8. Results of pre- and post-calibration of dissolved oxygen saturation.

			Pre-calibration Dissolved Oxygen % Saturation				Post-calibration Dissolved Oxygen % Saturation			
Field Use Date/s	Post-Check Date	Sonde #	Reference standard value	Hydrolab check value (after calibration)	Difference		Reference standard value	Hydrolab check value (post deployment)	Difference	
August 14-19, 2015	8/19/2015	34	100%	100.0%	0.0%	accept	100	99.5	-0.5%	accept
October 15-21, 2015	10/19/2015	31	100%	100.2%	0.2%	accept	100	99.4	-0.6%	accept
April 25-28, 2016	4/28/2016	41	100%	100.9%	0.9%	accept	100	100.4	0.4%	accept

QA of the Okanogan Conservation District alkalinity monitoring data

The Okanogan CD monitoring was conducted under a QA Project Plan which cited their *Water Quality Monitoring Standard Operating Procedure* (SOP) in regards to sampling protocols and instrument calibration. The QA Project Plan and SOP were reviewed by Ecology as part of the grant approval. Both documents were deemed in good standing and complete for the purposes of collecting water quality data.

The Okanogan CD's SOP lists pre-calibration procedures for the pH meter, as well as quality control measures to be performed throughout the sample day. Even though the QA Project Plan stated that a QA summary would be presented in the final report, the Okanogan CD final summary report (Bard, 2003) has no QA section or discussion. As significant time has lapsed, the Okanogan CD no longer has QA records pertaining to the monitoring project, so Ecology does not have documentation of QA for their monitoring activities from the 2000-2003 monitoring project.

A few duplicate pairs of alkalinity samples were taken by the Okanogan CD during their monitoring project. Table A-9 shows the duplicate pairs and their QA assessment. The precision of the duplicates was very good with a RMSE of 1.7 mg/L and a pooled coefficient of variation of 1.1%.

Table A-9. Quality assurance analysis of Okanogan CD alkalinity duplicate pairs.

Station	Date	Alkalinity (mg/L)	Alkalinity (mg/L)	Residual	
LOSINLAHEKINCR	7/10/2002	124	125	-1	
LOBONAPARTECR	8/14/2002	250	252	-2	
UPSINLAHEKINCR	9/12/2002	121	122	-1	
UPSINLAHEKINCR	10/10/2002	130	130	0	
UPBONAPARTECR	11/13/2002	116	116	0	
UPPERTUNKCR	12/10/2002	161	161	0	
UPBONAPARTECR	1/16/2003	128	129	-1	
UPPERTUNKCR	2/11/2003	147	151	-4	
			148.25	-1.125	Mean
				1.70	RMSE
				1.1%	CV%

Appendix B. pH modeling

Saturated pH levels were simulated using a modified pH model from the QUAL2Kw water quality model (Pelletier et al, 2006; Pelletier and Chapra, 2008). The modified model determines the pH saturation in freshwater by using the saturated CO_2 concentration.

The CO_2 saturation is computed with Henry's law,

$$[CO_2]_s = K_H p_{CO_2} \quad \textbf{(1)}$$

where K_H = Henry's constant [mole (L atm)$^{-1}$] and p_{CO_2} = the partial pressure of carbon dioxide in the atmosphere [atm]. The partial pressure is input to the model in units of ppm and the model internally converts ppm to atm using the conversion: 10^{-6} atm/ppm. The value of K_H can be computed as a function of temperature by (Edmond and Gieskes 1970)

$$pK_H = -\frac{2385.73}{T_a} - 0.0152642 T_a + 14.0184 \quad \textbf{(2)}$$

The partial pressure of CO_2 in the atmosphere has been increasing (Figure B-1). Values in 2016 are approximately 407 ppm.

The following equilibrium, mass balance and electroneutrality equations define a freshwater dominated by inorganic carbon (Stumm and Morgan 1996),

$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \quad \textbf{(3)}$$

$$K_2 = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \quad \textbf{(4)}$$

$$K_w = [H^+][OH^-] \quad \textbf{(5)}$$

$$c_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad \textbf{(6)}$$

$$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad \textbf{(7)}$$

where K_1, K_2 and K_w are acidity constants, *Alk* = alkalinity [eq L^{-1}], $H_2CO_3^*$ = the sum of dissolved carbon dioxide and carbonic acid, HCO_3^- = bicarbonate ion, CO_3^{2-} = carbonate ion, H^+ = hydronium ion, OH^- = hydroxyl ion, and c_T = total inorganic carbon concentration [mole L^{-1}]. The brackets [ ] designate molar concentrations.

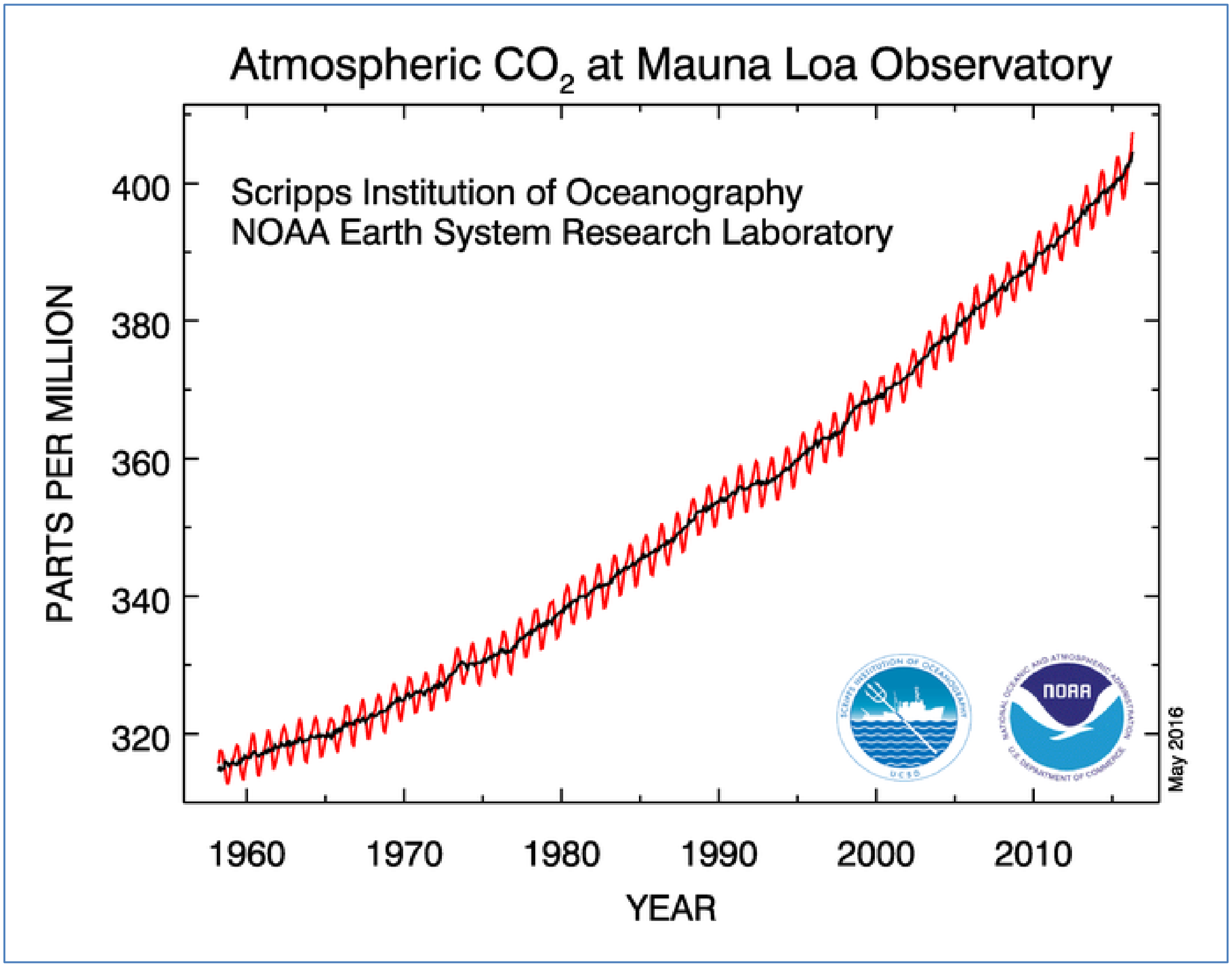

Figure B-1. Concentration of carbon dioxide in the atmosphere as recorded at Mauna Loa Observatory, Hawaii. (http://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png) - accessed on 5/20/2016.

Alkalinity is expressed in units of eq/L for the internal calculations. For input and output, it is expressed as $mgCaCO_3/L$. The two units are related by

$$Alk(\mathrm{mgCaCO_3/L}) = 50{,}043.45 \times Alk(\mathrm{eq/L}) \tag{8}$$

The equilibrium constants are corrected for temperature by

Harned and Hamer (1933):

$$\mathrm{p}K_w = \frac{4787.3}{T_a} + 7.1321\log_{10}(T_a) + 0.010365T_a - 22.80 \tag{9}$$

Plummer and Busenberg (1982):

$$\log K_1 = -356.3094 - 0.06091964T_a + 21834.37/T_a + 126.8339\log T_a - 1{,}684{,}915/T_a^2 \tag{10}$$

Plummer and Busenberg (1982):

$$\log K_2 = -107.8871 - 0.03252849T_a + 5151.79/T_a + 38.92561\log T_a - 563{,}713.9/T_a^2 \tag{11}$$

The nonlinear system of five simultaneous equations (3 through 7) can be solved numerically for the five unknowns: $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, $[OH^-]$, and $\{H^+\}$. An efficient solution method can be derived by combining Eqs. (3), (4) and (6) to define the quantities (Stumm and Morgan 1996)

$$\alpha_0 = \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{12}$$

$$\alpha_1 = \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{13}$$

$$\alpha_2 = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \tag{14}$$

where α_0, α_1, and α_2 = the fraction of total inorganic carbon in carbon dioxide, bicarbonate, and carbonate, respectively. Equations (5), (7), (13) and (14) can then be combined to yield,

$$\text{Alk} = (\alpha_1 + 2\alpha_2)\frac{[CO_2]_s}{\alpha_0} + \frac{K_w}{[H^+]} - [H^+] \tag{15}$$

Thus, solving for pH when the dissolved CO_2 equals $[CO_2]_s$ reduces to determining the root,

$\{H^+\}$, of

$$f([H^+]) = (\alpha_1 + 2\alpha_2)\frac{[CO_2]_s}{\alpha_0} + \frac{K_w}{[H^+]} - [H^+] - \text{Alk} \tag{16}$$

where pH is then calculated with

$$\text{pH} = -\log_{10}[H^+] \tag{17}$$

The root of Eq. (16) is determined with the Brent numerical method (Brent, 1973) in the pH model. The pH model was written in VBA and runs in Excel©.

References for Appendix B

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Appendix C. Alkalinity data collected by the Okanogan Conservation District

The Okanogan Conservation District (CD) collected alkalinity data on Tunk, Sinlahekin, and Bonaparte Creeks from May 2000 to May 2003. Two of the creeks, Tunk and Sinlahekin, were tributaries that the verification study found pH levels above the 8.5 upper pH criterion. The verification study did not find pH levels above criteria in Bonaparte Creek, but monitoring by Ecology's Freshwater Monitoring Unit (FMU) did measure exceedances (see Appendix D). In each tributary there were seasonal variation to alkalinity concentrations as shown in Figure C-1.

pH saturation was calculated for all of the verification study tributaries with pH levels over the upper pH criterion of 8.5 pH units, as well as Bonaparte Creek (Appendix D). Since alkalinity was not measured for the verification study, either a regression to conductivity was used to estimate the alkalinity or the monthly average alkalinity from the 2000-2003 data was used as an estimate of the alkalinity in the pH saturation model. Table C-1 presents a summary of the alkalinity data. Bolded values were used in the pH model.

Table C-1. Summary of alkalinity data used in the calculation of pH saturation.

Tributary	August 2000-03 mean alkalinity	October 2000-03 mean alkalinity	April 2000-03 mean alkalinity	August 2015 alkalinity from regression	October 2015 alkalinity from regression	April 2016 alkalinity from regression
Bonaparte Creek (lower)	**245**	235	188	212	**186**	**75**
Siwash Creek (lower)	NA	NA	NA	**226**	**226**	**153**
Johnson Creek (lower)	NA	NA	NA	**208**	**189**	**199**
Tunk Creek (lower)	194	212	**123**	**140**	**162**	50
Chiliwist Creek (lower)	NA	NA	NA	**45-152**	**145**	**145**
Sinlahekin Creek (upper)	**111**	**139**	143	93	NA	**62**

Figure C-2 shows the regression between conductivity and alkalinity data collected by the Okanogan CD. The correlation was also compared to groundwater measurements of alkalinity and conductivity in the Okanogan basin published by the USGS (1984). As shown in the top figure, the relationship above 600 umhos/cm becomes indistinct and uncertain. This assessment used a relationship that was cut off at conductivities greater than 600 umhos/cm (bottom figure) because the conductivities of waters that this verification study used to calculate pH saturation were less than 600 umhos/cm.

The linear regression equation, developed from the Okanogan CD surface water data only, predicts alkalinity expressed in mg/L of $CaCO_3$ to be about 37% of the numerical value of specific conductivity expressed as umhos/cm. The linear model has a pooled RMSE (n=135) for the alkalinity prediction of ±29.3 mg/L with a pooled bias of 0.4 mg/L and coefficient of variation (CV) of 17.7%.

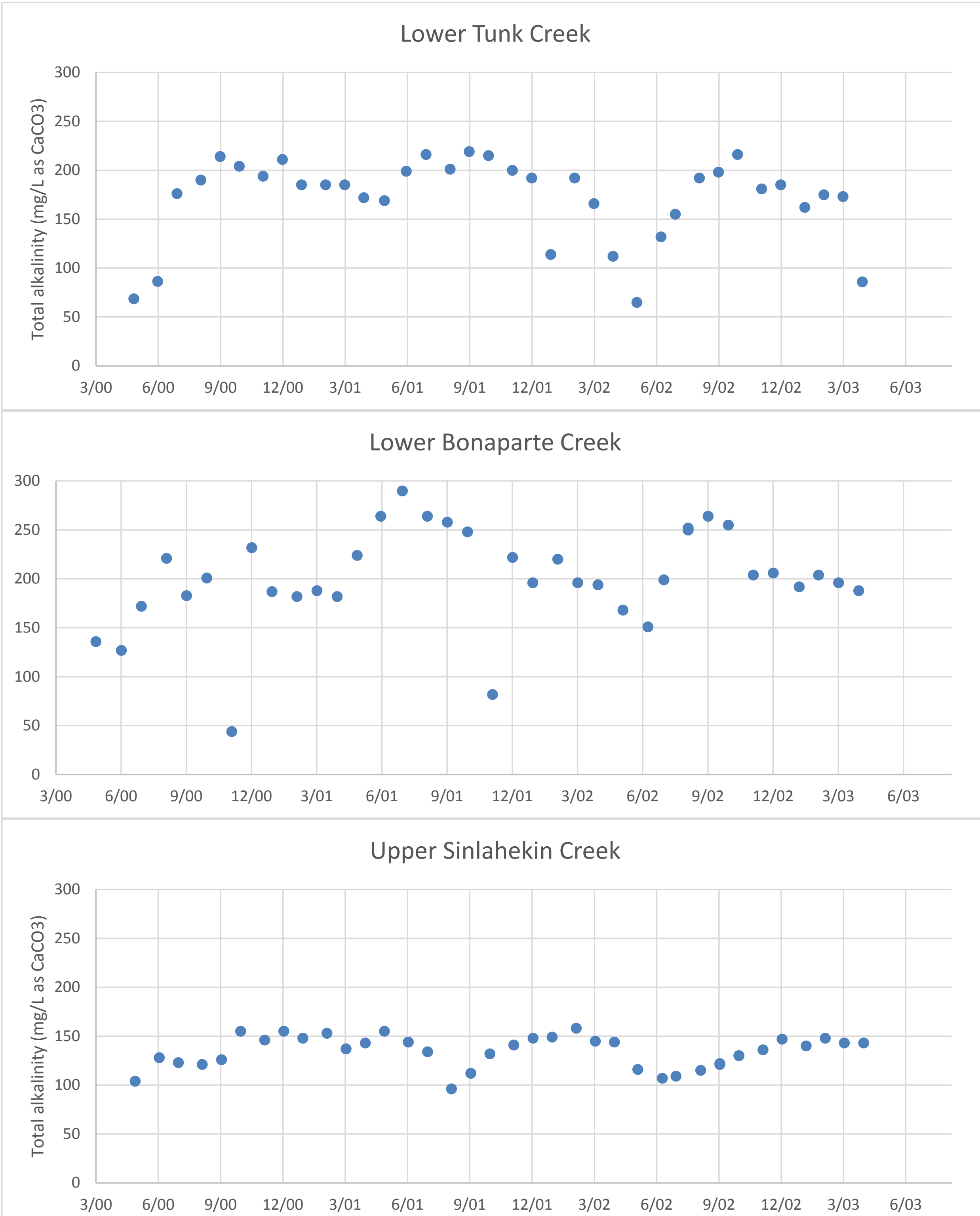


Figure C-1. Total alkalinity results from the Okanogan CD monitoring in 2000-2003.

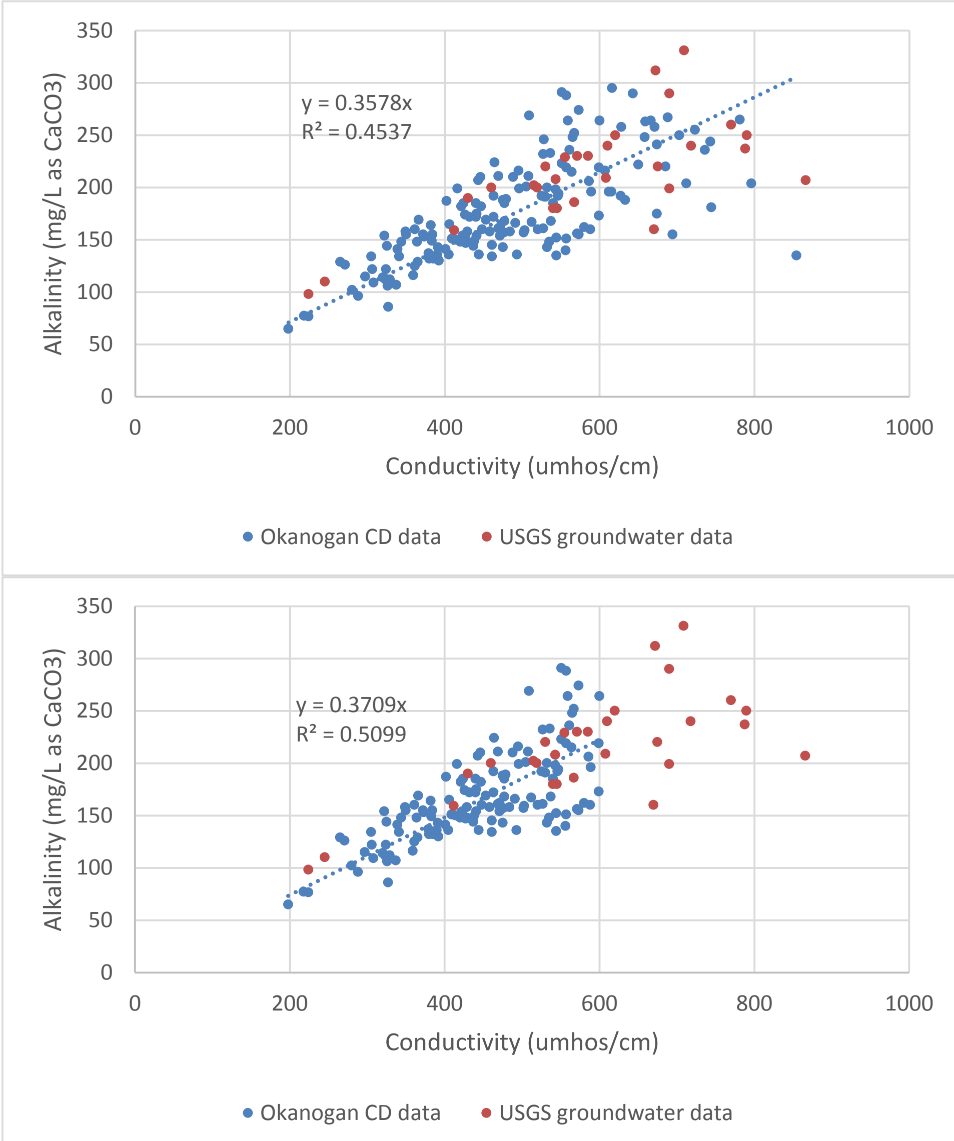


Figure C-2. Regression between conductivity and alkalinity using Okanogan CD surface water data and showing relationship to USGS groundwater data for the Okanogan basin.

Appendix D. Bonaparte Creek monitoring by Ecology's Freshwater Monitoring Unit

Ecology's Freshwater Monitoring Unit (FMU) samples Bonaparte Creek monthly as part of a statewide monitoring program. Bonaparte Creek is scheduled to be monitored monthly from October 2014 to September 2016. Most of FMU instantaneous measurements of pH have been taken around 10:00 am in the morning and many have exceeded the 8.5 maximum criterion of the water quality standards (Table D-1).

A comparison of FMU monitoring of Bonaparte Creek to the verification monitoring is shown in Figure D-1. Even when measurements were made close in time, the verification study had pH measurements below the FMU pH measurements:

- A measurement was made 2 days after the verification study's continuous measurements on October 17, 2015. Even though this study did not show any measurements above 8.37, the FMU reading was 8.56.
- Also, in August 2015, FMU measured a pH reading of 8.50 when the highest measured by this study was 8.42. These are very slight differences and within the measurement error commonly associated with measuring pH.

However small the differences though, they are the difference between being in or out of compliance with the state water quality pH criteria.

Both the verification study and the FMU records of quality assurance and quality control (QA/QC) documentation show that both pH meter were well calibrated and accurately reading pH, and the measurement error was acceptable within the measurement quality objectives.

However, FMU uses a different methodology for measuring pH than what was used for the verification study. While the verification study measured pH "in situ" (in the creek) with a datalogger recording every 30 minutes, the FMU measurement was made on a single sample of water taken out of the creek and put into a sample cup in the FMU van. The pH measurement was recorded after allowing the pH reading to equilibrate, sometimes for several minutes, after stirring. This sampling methodology likely introduces a bias by letting the sample equilibrate to the atmosphere before measurement.

FMU does not sample for alkalinity normally. Estimates of pH saturation were made using the regression between conductivity and alkalinity (Appendix C). Figure D-2 shows the calculated pH saturation for each of the FMU pH measurements. Often the FMU measurement and pH saturation were near the same. Figure D-3 shows the verification pH measurements in comparison to the pH saturation. Mostly, the pH verification measurements showed under-saturated pH levels that paralleled the pH saturation time concentration curve, with de minimis indication (<= 0.10 diel amplitude) of biological activity indicating an equilibrium condition.

The FMU ambient monitoring program is designed to be a screening program. If monitoring shows a station out of compliance with pH criteria, a determination needs to be made whether the water is impaired due to anthropogenic causes or if the high pH is due to natural causes. This verification study concludes that Bonaparte Creek does not have a exceedance of the pH criteria.

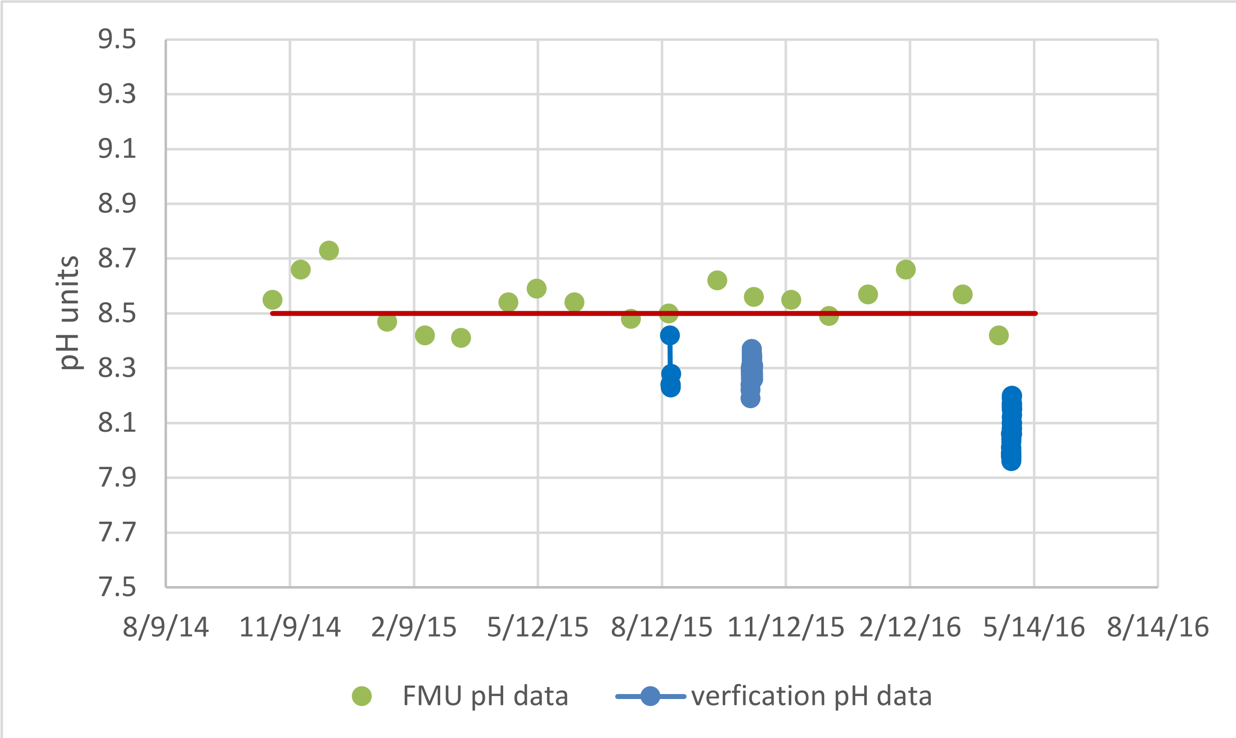


Figure D-1. A comparison of FMU pH monitoring of Bonaparte Creek to the continuous in situ pH monitoring from the verification study.

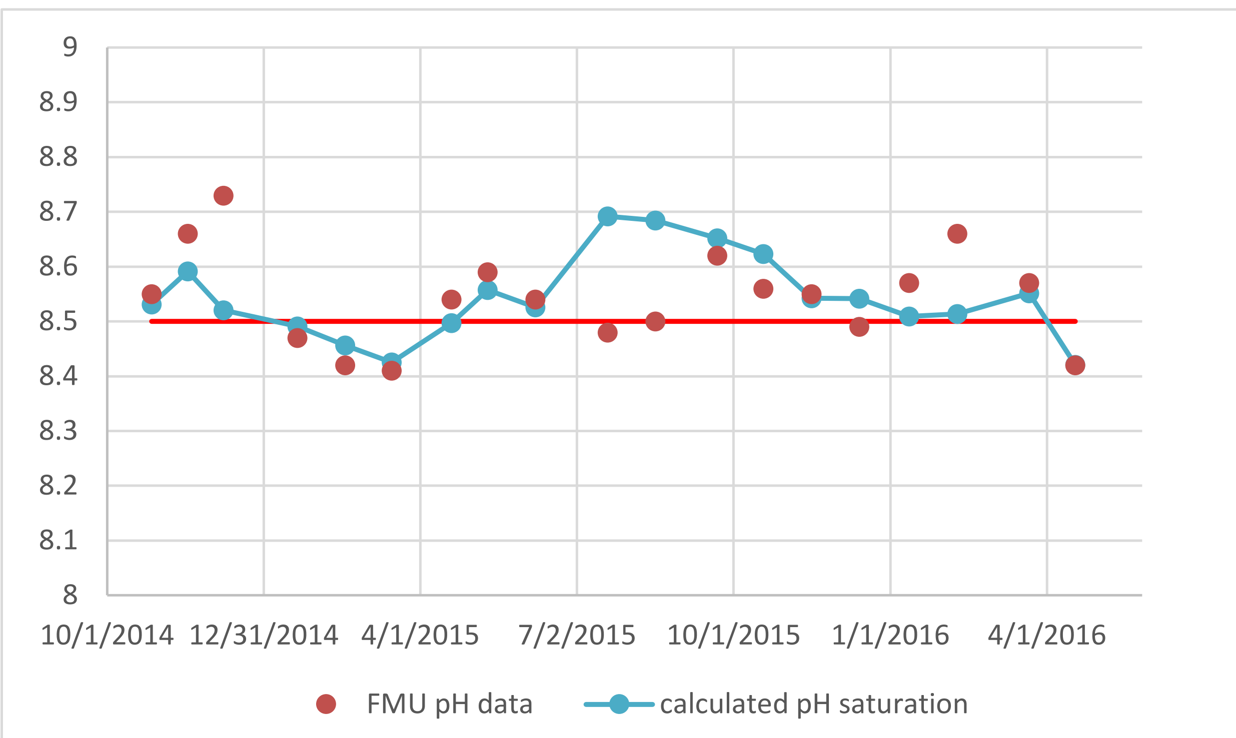


Figure D-2. A comparison of FMU pH monitoring of Bonaparte Creek to calculated pH saturation.

Table D-1. Preliminary FMU results from Bonaparte Creek @ Tonasket (station 49F070).

Caution: Data are not considered finalized until our annual report is published. This can take as long as nine months from the end of the water year. Until published, data are subject to change.

date	time	COND (umhos/cm)		NH3_N (mg/L)		NO2_NO3 (mg/L)		OP_DIS (mg/L)		OXYGEN (mg/L)		PH (pH)		SUSSOL (mg/L)		TEMP (deg C)		TP_P (mg/L)		TURB (NTU)	
10/27/2014	09:55	438		0.013		0.010	U	0.0596		11.7		8.55		16		6.8		0.0755		7.5	
11/17/2014	10:17	545		0.010	U	0.012		0.0603		13.9		8.66		1	U	0		0.0617		0.5	U
12/8/2014	10:27	448		0.010	U	0.133		0.0483		13.3		8.73		5		1.3		0.0554		2.5	
1/20/2015	09:59	418		0.01	U	0.195		0.0483		14.1		8.47		5		0		0.0545		2.7	
2/17/2015	10:20	379		0.015		0.172		0.0489		13.5		8.42		28		1.3		0.0885		11	
3/16/2015	10:02	340		0.01	U	0.023		0.0399		12.2		8.41		175	J	4.4		0.209		55	
4/20/2015	10:15	389		0.01	U	0.01	U	0.0483		10.7		8.54		18		9.5		0.0755		6.8	
5/11/2015	10:23	438		0.01	U	0.01	U	0.0663		10.2		8.59		6		13		0.0797		2.9	
6/8/2015	10:12	377		0.011		0.05		0.0863		8.7		8.54		37		18.2		0.139		14	
7/20/2015	09:59	545		0.014		0.013		0.0941		8.6		8.48		2	U	24.1		0.0956		1.1	
8/17/2015	10:02	569		0.01	U	0.01	U	0.0681		8.9		8.50		1		19.5		0.0692		0.7	
9/22/2015	10:24	573		0.01	U	0.01	U	0.101		10.5		8.62		1		11.9		0.102		1.3	
10/19/2015	10:22	530		0.01	U	0.01	U	0.0924		9.9		8.56		2		11.8		0.0951		1	
11/16/2015	10:26	465		0.01	U	0.01	U	0.0528		12.6		8.55		4		3.6		0.0656		2.3	
12/14/2015	09:43	470		0.010	U	0.202		0.0488		13		8.49		8		2.2		0.0706		4.3	
1/12/2016	09:40	435		0.01	U	0.203		0.0421		13.3		8.57		3		1.2		0.0567		1.1	
2/9/2016	09:30	443		0.01	U	0.065		0.0263		13.9		8.66		3		0.3		0.0302		1.4	

Common data qualifiers: U - not detected at the reported level, J - estimated value
Times are local (Pacific Standard or Pacific Daylight Savings).
Colored background indicates that result exceeded water quality standards -OR- contrasted strongly with historical results. The November 2006 amendment to the water quality standards was incorporated beginning in January 2009.

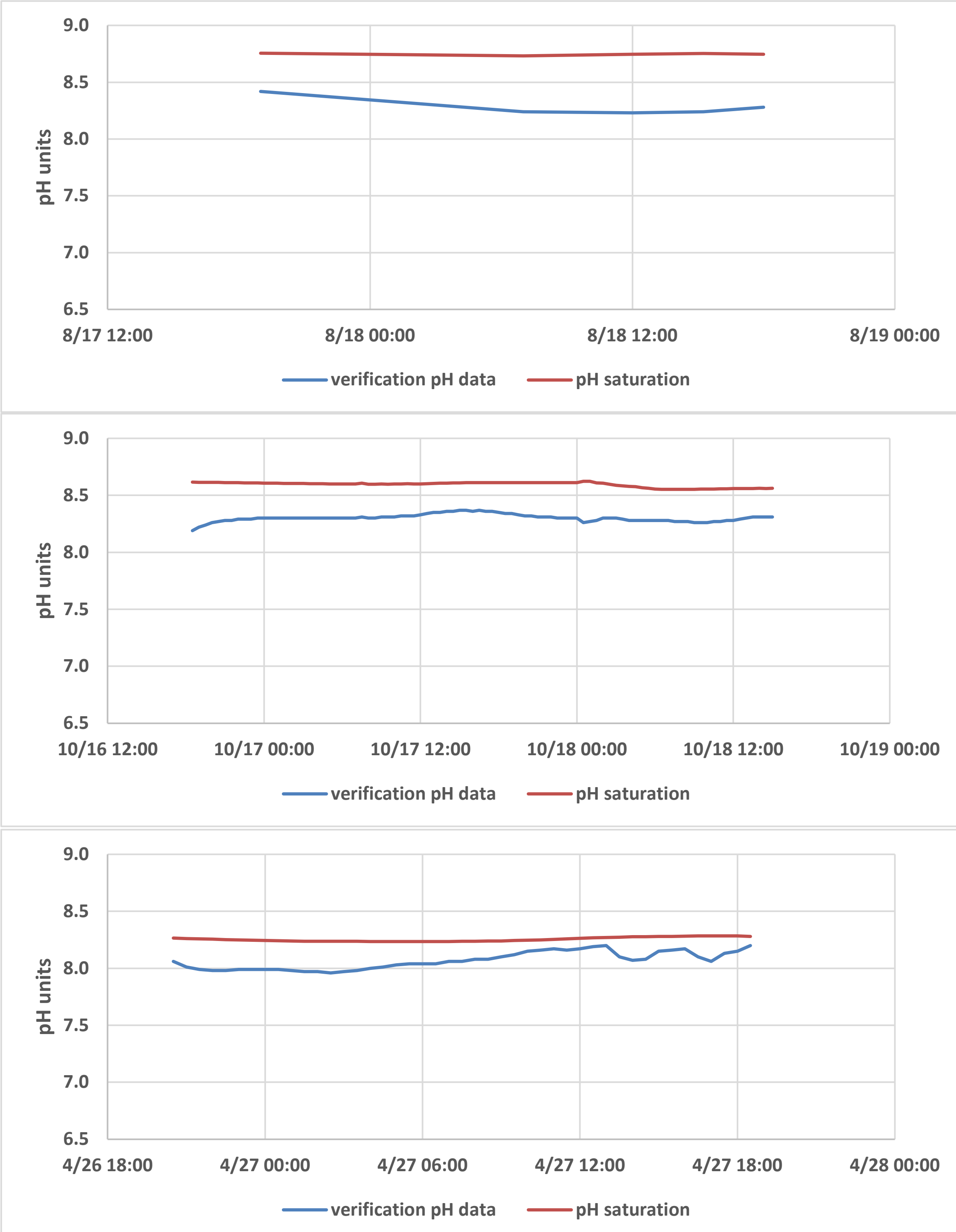
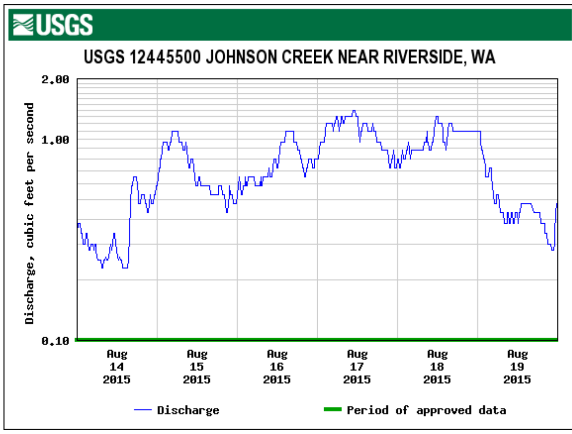
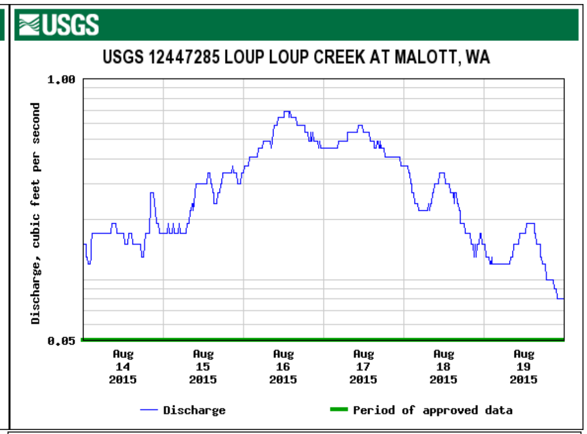
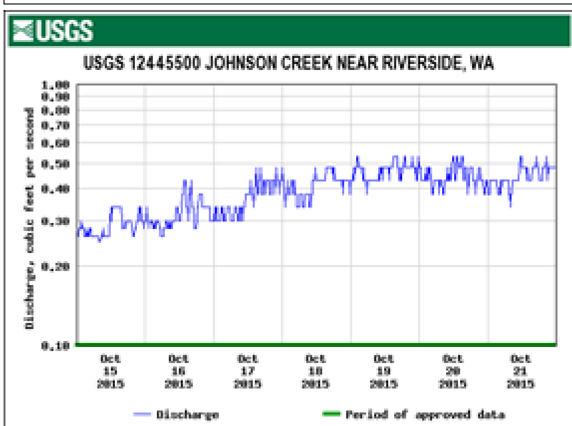


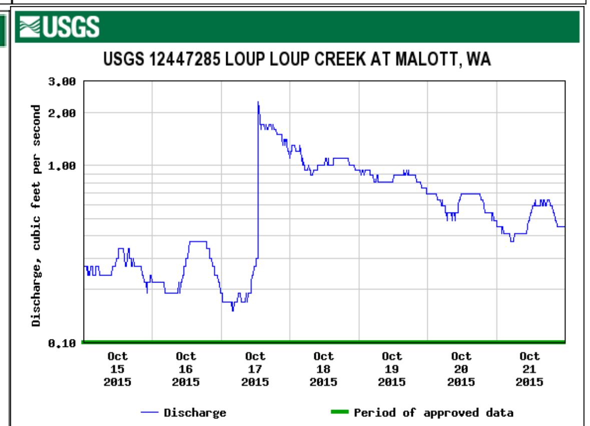
Figure D-3. Results of pH time series for Bonaparte Creek verification monitoring in August and October 2015 and April 2016 compared to the pH saturation.

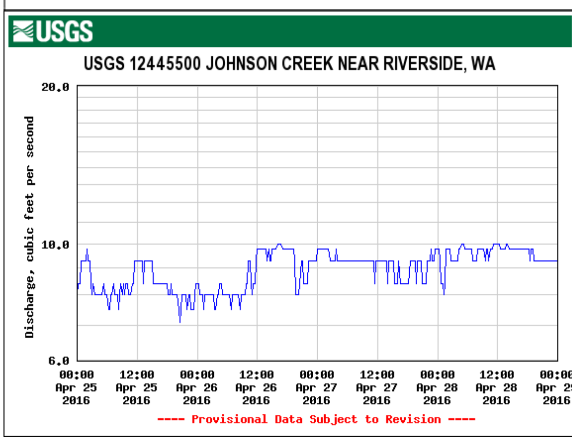
Appendix E. Streamflow data from USGS

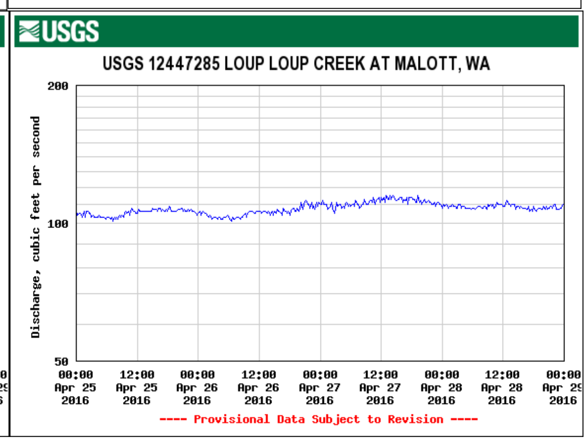


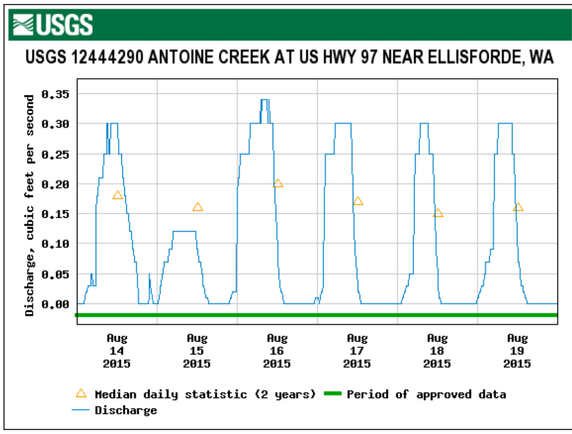


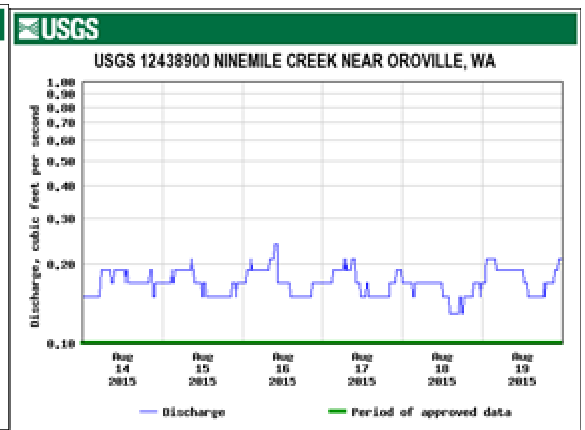









USGS
USGS 12444290 ANTOINE CREEK AT US HWY 97 NEAR ELLISFORDE, WA
Discharge, cubic feet per second
Aug 14 2015
Aug 15 2015
Aug 16 2015
Aug 17 2015
Aug 18 2015
Aug 19 2015
Median daily statistic (2 years)
Period of approved data
Discharge


USGS
USGS 12438900 NINEMILE CREEK NEAR OROVILLE, WA
Discharge, cubic feet per second
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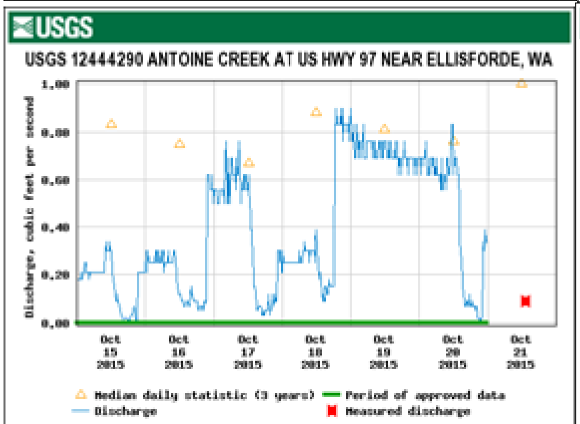
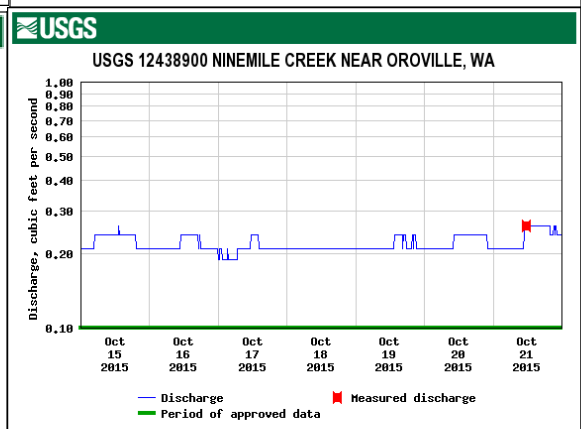
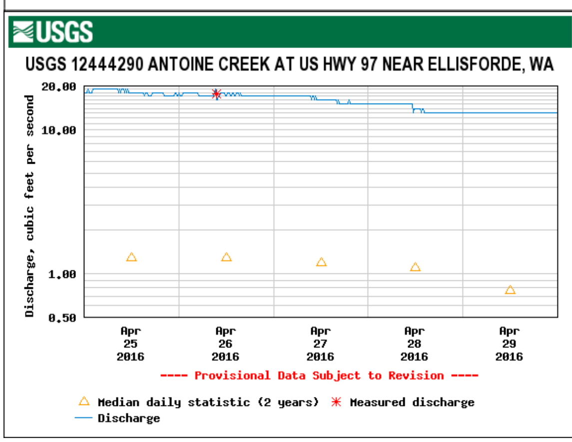
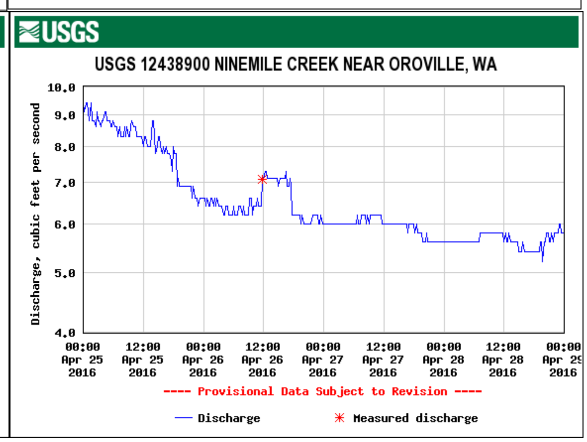
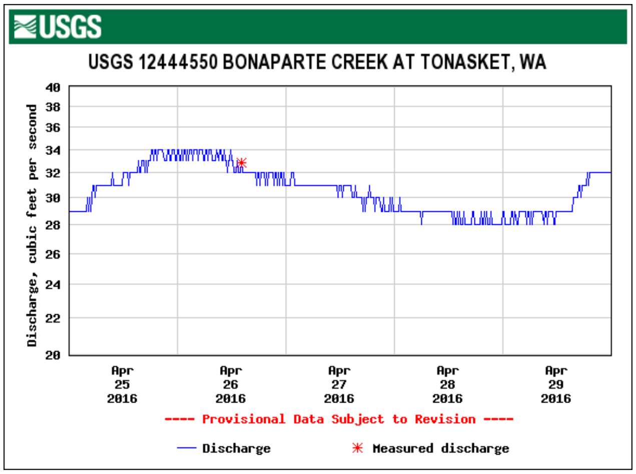
Aug 15 2015
Aug 16 2015
Aug 17 2015
Aug 18 2015
Aug 19 2015
Discharge
Period of approved data


USGS
USGS 12444290 ANTOINE CREEK AT US HWY 97 NEAR ELLISFORDE, WA
Discharge, cubic feet per second
Oct 15 2015
Oct 16 2015
Oct 17 2015
Oct 18 2015
Oct 19 2015
Oct 20 2015
Oct 21 2015
Median daily statistic (3 years)
Period of approved data
Discharge
Measured discharge


USGS
USGS 12438900 NINEMILE CREEK NEAR OROVILLE, WA
Discharge, cubic feet per second
Oct 15 2015
Oct 16 2015
Oct 17 2015
Oct 18 2015
Oct 19 2015
Oct 20 2015
Oct 21 2015
Discharge
Measured discharge
Period of approved data


USGS
USGS 12444290 ANTOINE CREEK AT US HWY 97 NEAR ELLISFORDE, WA
Discharge, cubic feet per second
Apr 25 2016
Apr 26 2016
Apr 27 2016
Apr 28 2016
Apr 29 2016
---- Provisional Data Subject to Revision ----
Median daily statistic (2 years)
Measured discharge
Discharge


USGS
USGS 12438900 NINEMILE CREEK NEAR OROVILLE, WA
Discharge, cubic feet per second
---- Provisional Data Subject to Revision ----
Discharge
Measured discharge


USGS
USGS 12444550 BONAPARTE CREEK AT TONASKET, WA
Discharge, cubic feet per second
40
38
36
34
32
30
28
26
24
22
20
Apr 25 2016
Apr 26 2016
Apr 27 2016
Apr 28 2016
Apr 29 2016
---- Provisional Data Subject to Revision ----
Discharge
Measured discharge

Appendix F. Verification of 303(d)-listed tributaries for dissolved oxygen.

Three tributaries are on the 2012 303(d) list for dissolved oxygen (DO). Table F-1 lists the tributaries and the DO criteria. In addition, upper Loup Loup Creek is on the current 303(d) list for DO (Table F-2).

Ninemile and Sinlahekin Creeks have a DO criterion of 9.5 mg/L because they discharge to lakes. The upper Loup Loup Creek reach has a 9.5 mg/L criterion because it is located on US Forest Service property. It is likely that some of the sites with a DO criterion of 9.5 mg/L may have DO levels below the criterion because the DO saturation is below the criterion.

Table F-1. DO listings on 2012 303(d) list.

Tributary ID	2012 dissolved oxygen 303(d) listings for tributaries		
	pH	DO	DO criteria
LOSINLAHEKINCR	no	yes	9.5
UPSINLAHEKINCR	yes	yes	9.5
LONINEMILECR	yes	yes	9.5
UPNINEMILECR	yes	yes	9.5
UPTONASKETCR	yes	yes	8

Table F-2. New DO listing on current 303(d) list.

Tributary ID	Current dissolved oxygen 303(d) listings for tributaries		
	pH	DO	DO criteria
UPLOUPLOUPCR	no	yes	9.5

The data used for listing the tributaries were mostly collected by the Okanogan CD from 2000-2003. Like the pH data collected by them, the DO data does not have a quality assurance (QA) records. There is no existing documentation of calibration records or quality control procedures, therefore the data is not suitable for assessment of DO conditions.

Analysis of listed tributaries for DO

Despite the lack of QA records, the Okanogan CD data were compared to DO saturation levels below to see how close the measurements were to saturation.

Lower Sinlahekin Creek

Figure F-1 shows the DO data collected by the Okanogan CD in comparison to DO saturation levels. The Okanogan CD data were generally near saturation, with exceptions in 2002, when the data may be anomalous. DO saturation is expected to be below the 9.5 mg/L criterion in the summer months when the stream is warmer. The lower Sinlahekin Creek site was not monitored during the verification study, so no new data could be assessed.

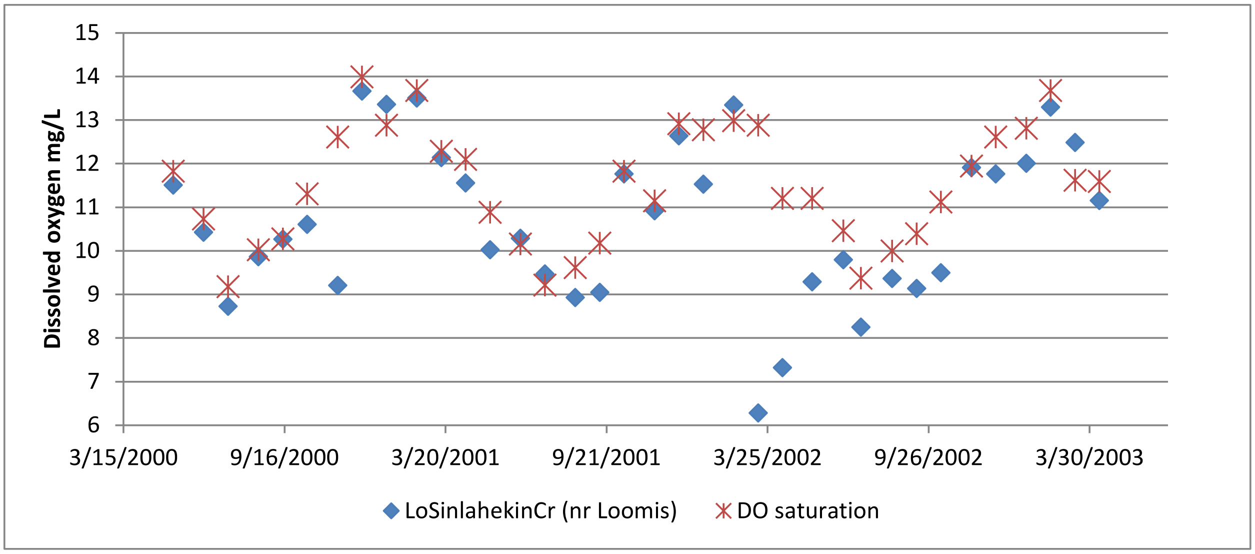


Figure F-1. Okanogan CD dissolved oxygen data compared to saturated levels for lower Sinlahekin Creek.

Upper Sinlahekin Creek

DO data collected by the Okanogan CD were generally near saturation, with exceptions in 2002, which may be anomalous data (Figure F-2). DO saturation is expected to be below the 9.5 mg/L criterion in the summer months when the stream is warmer.

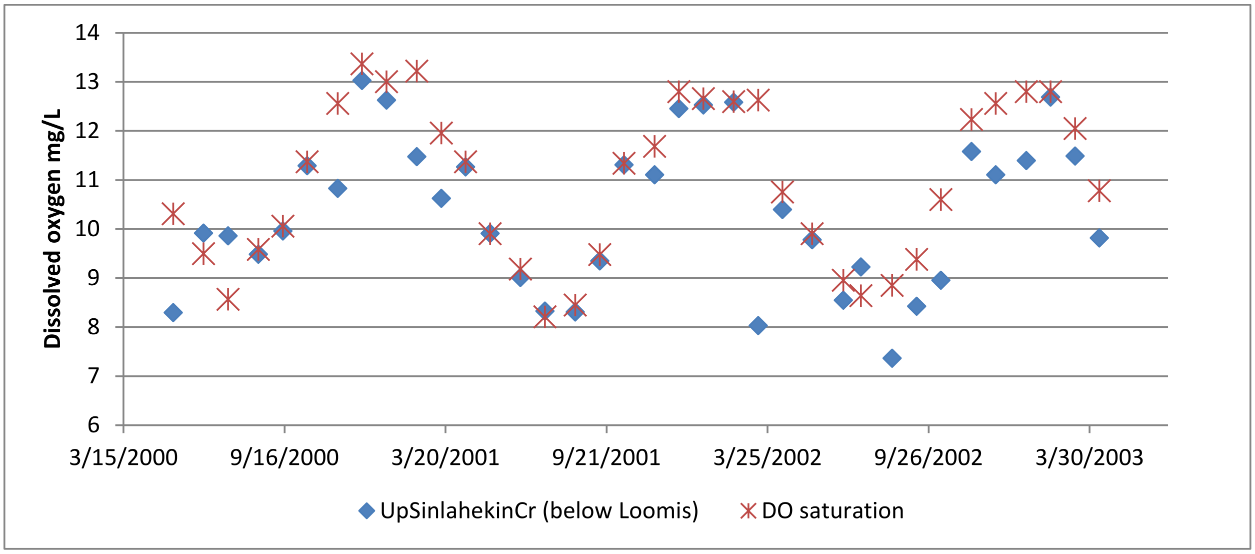


Figure F-2. Okanogan CD dissolved oxygen data compared to saturated levels for upper Sinlahekin Creek.

During the verification study, the upper Sinlahekin Creek site was monitored at a different location about 2 miles downstream from the listed site. DO data were not collected in August or October 2015. However, the calculated DO saturation based on the elevation of the site and the water temperature in August 2015 was below the 9.5 criteria for the entire day (Figure F-3). The water temperature may be elevated due to anthropogenic reasons, and the site is also listed for pH and water temperature exceeding criteria. DO data collected in April 2016 showed the observed DO data at saturation levels and within criteria (Figure F-4).

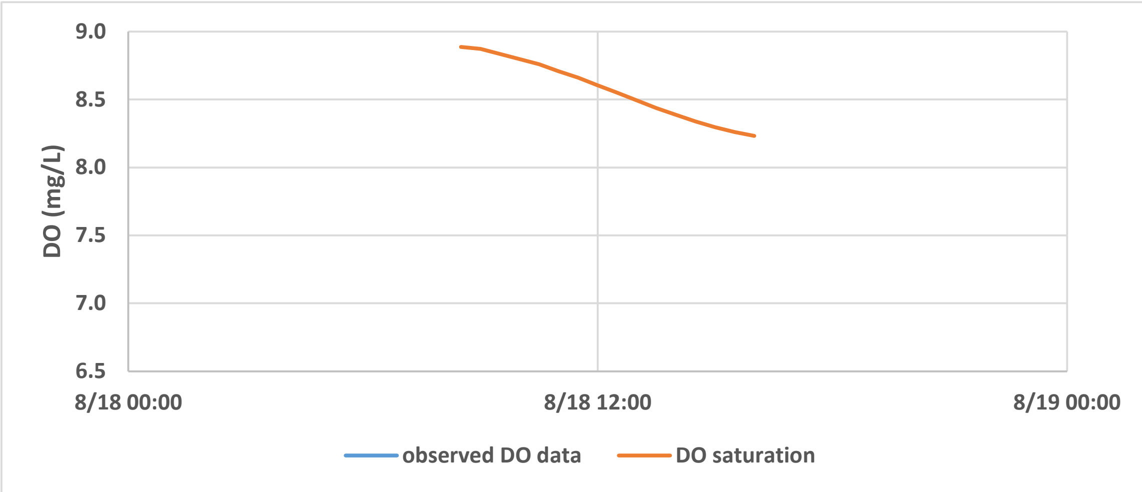


Figure F-3. DO saturation levels in upper Sinlahekin Creek during the verification study in August 2015.

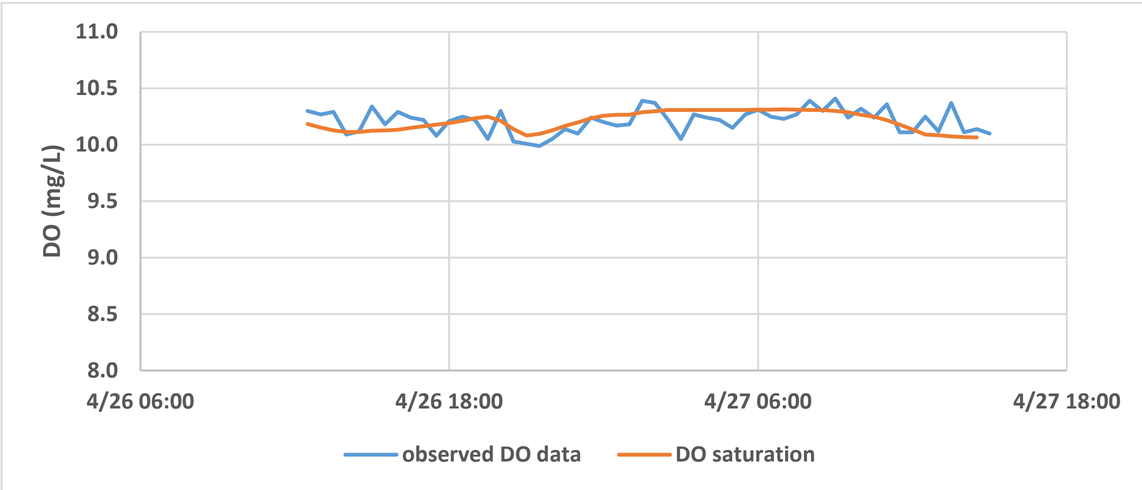


Figure F-4. Verification study DO monitoring data compared to saturation levels in upper Sinlahekin Creek during April 2016.

Lower Ninemile Creek

DO data collected by the Okanogan CD were generally near saturation, with exceptions in 2002, which may be anomalous data. DO saturation is expected to be below the 9.5 mg/L criterion in the summer months when the stream is warmer.

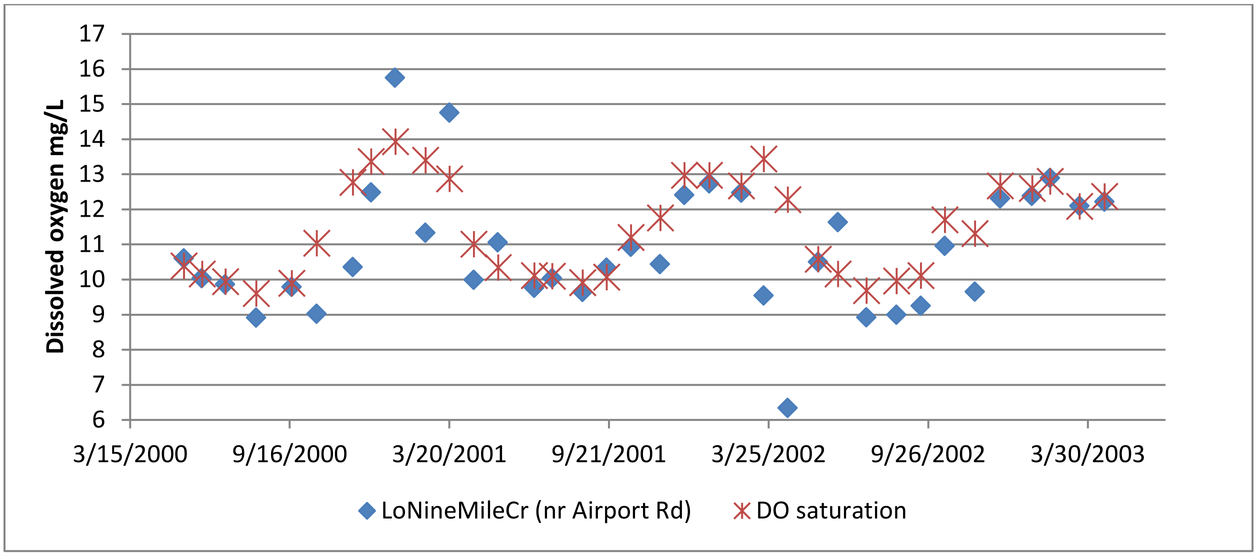


Figure F-5. Okanogan CD dissolved oxygen data compared to saturated levels for lower Ninemile Creek.

The lower Ninemile Creek site was monitored for DO during the pH verification study only in August and October 2015 (Figures F-6 and F-7). Like the pH monitoring data, the observed DO in the creek was just below saturation and showed no indication of biological activity that causes DO fluctuations throughout the day (<0.10 mg/L difference in diel amplitudes of saturated and observed DO). The DO saturation in August was below the 9.5 mg/L criterion established for the creek due to temperature and elevation at the location.

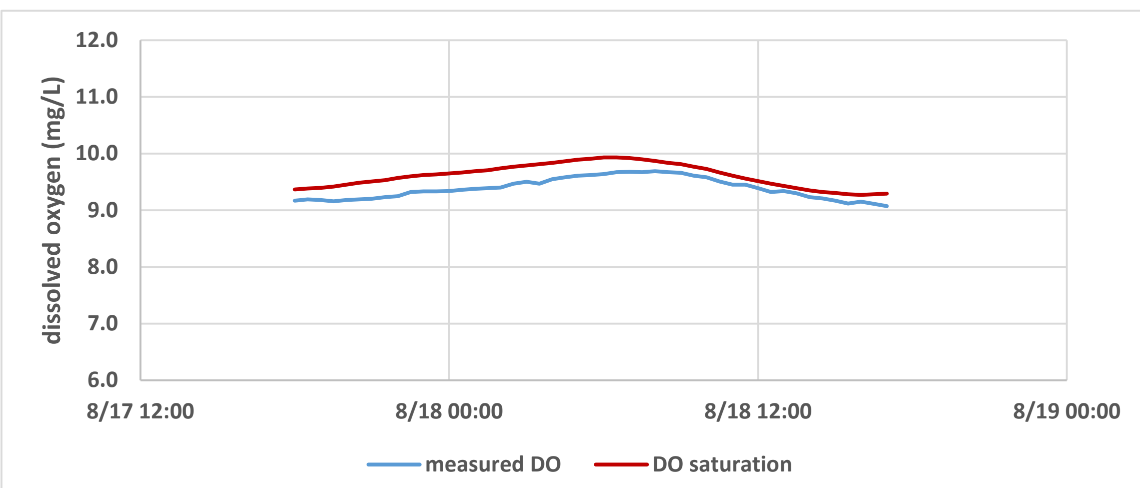


Figure F-6. Verification study dissolved oxygen data compared to saturated levels for lower Ninemile Creek in August 2015.

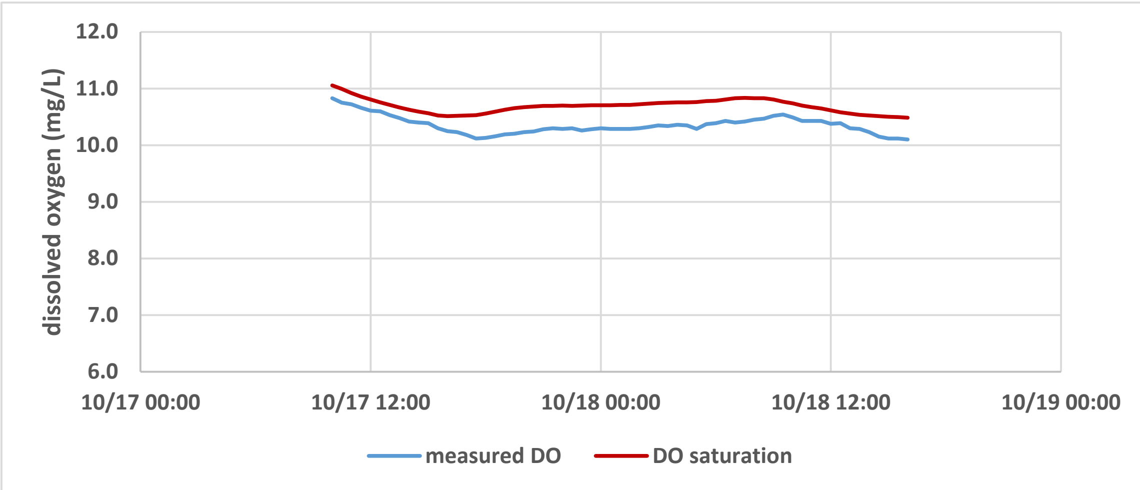


Figure F-7. Verification study dissolved oxygen data compared to saturated levels for lower Ninemile Creek in October 2015.

Upper Ninemile Creek

DO data collected by the Okanogan CD were generally at saturation (Figure F-8). The DO saturation is expected to be below the 9.5 mg/L criterion in the summer months when the stream is warmer. The upper Ninemile Creek site was not monitored during the verification study, so no new data could be assessed. However, the verification data at the lower Ninemile Creek site suggest there is no DO impairment in Ninemile Creek.

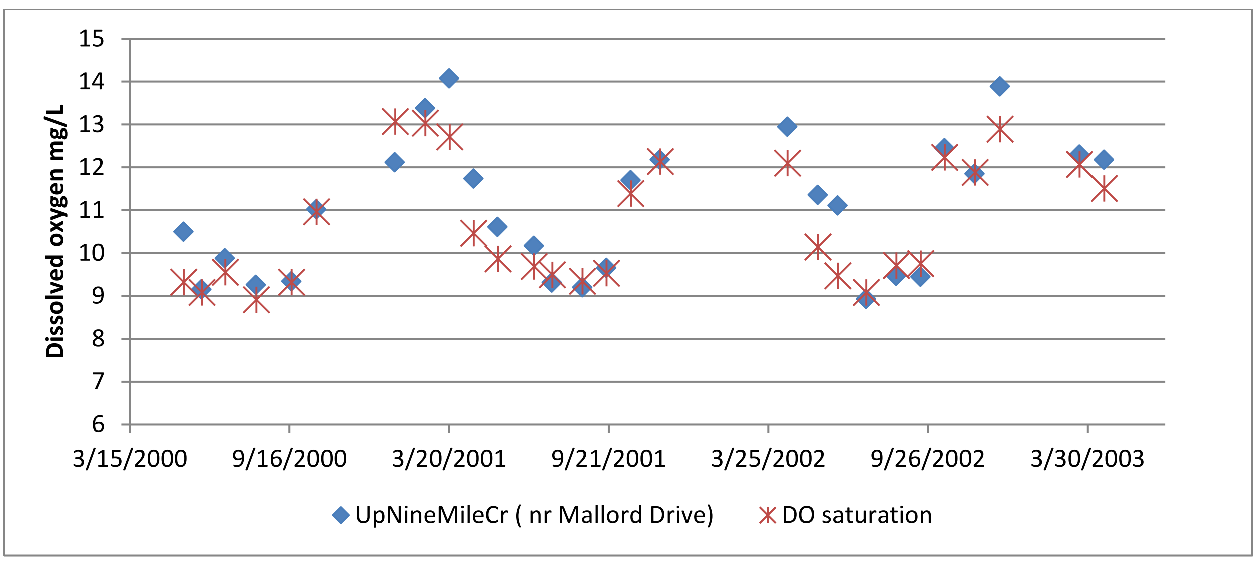


Figure F-8. Okanogan CD dissolved oxygen data compared to saturated levels for upper Ninemile Creek.

Upper Tonasket Creek

DO data collected by the Okanogan CD were generally at saturation (Figure F-9), except for once in the summers of 2001 and 2002. The low DO measurement in March of 2002 is probably erroneous. The calculated DO saturation was never below the 8.0 mg/L criterion. The upper Tonasket Creek site was not monitored during the verification study, so no new data could be assessed. However, the lower Tonasket Creek site did not show signs of biological activity based on a comparison of diel amplitudes of saturated and observed pH (<0.10 diel amplitude difference), and should be used as a proxy for biological activity at the upper Tonasket Creek site. This study therefore concludes that it is unlikely that Tonasket Creek has a DO impairment due to biological activity in the creek.

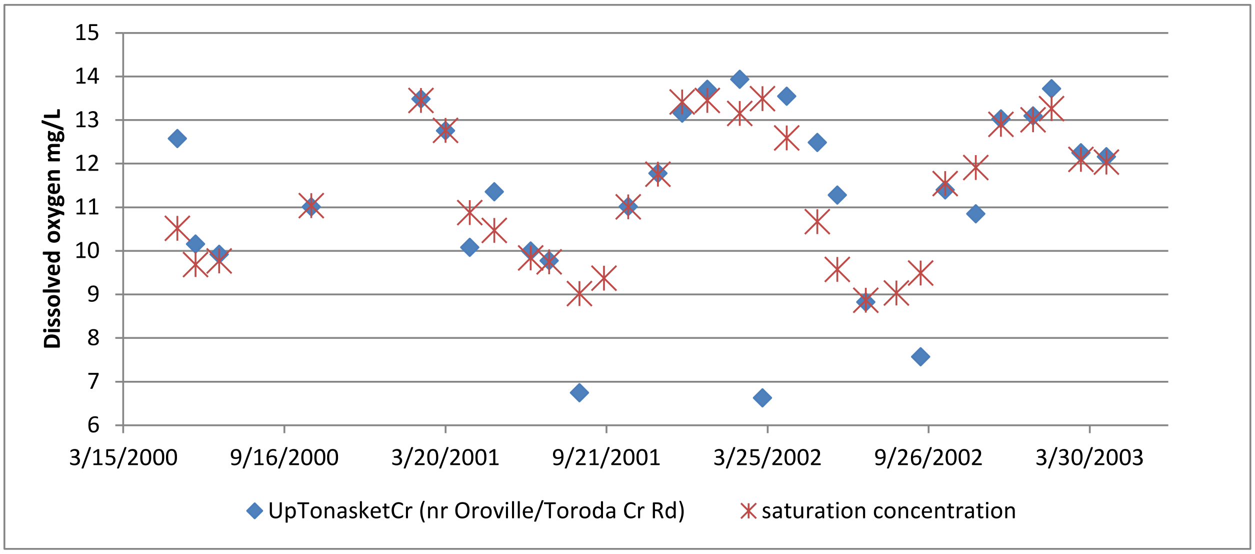


Figure F-9. Okanogan CD dissolved oxygen data compared to saturated levels for upper Tonasket Creek.

Upper Loup Loup Creek

DO data collected by the Okanogan CD were generally at saturation (Figure F-10), except for the summer of 2002. The DO saturation is expected to be below the 9.5 mg/L criterion in the summer months when the stream is warmer. The upper Loup Loup Creek site was not monitored during the verification study, so no new data could be assessed. However, the lower Loup Loup Creek site did not show signs of biological activity based on a comparison of diel amplitudes of saturated and observed pH (≈ 0.1 diel amplitude difference) and should be used as a proxy for biological activity at the upper Loup Loup Creek site. This study therefore concludes that it is unlikely that Loup Loup Creek has a DO impairment due to biological activity in the creek.

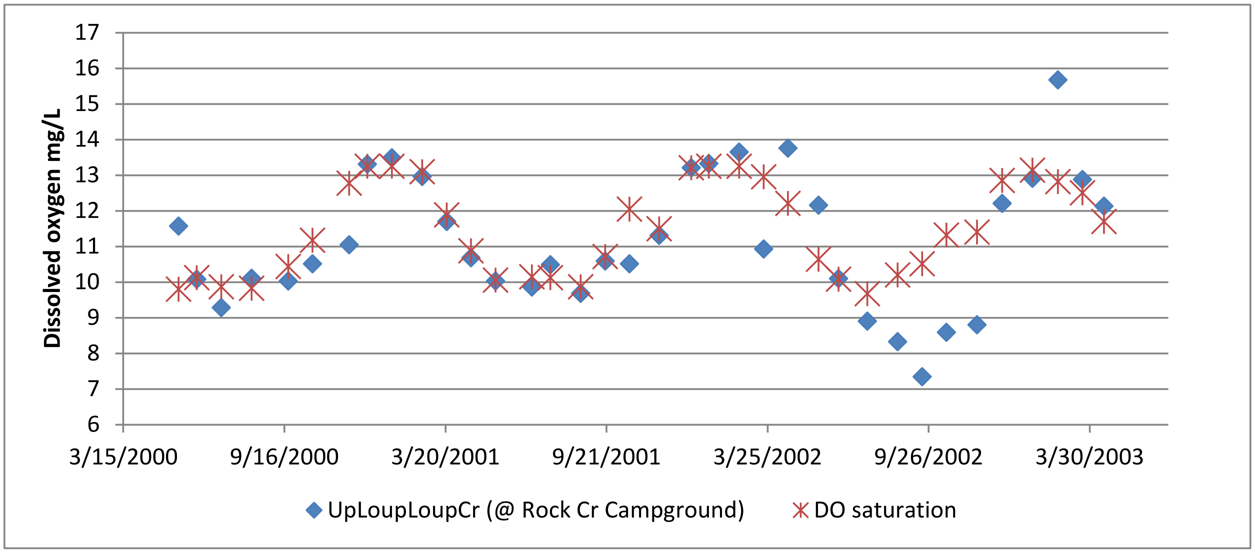


Figure F-10. Okanogan CD dissolved oxygen data compared to saturated levels for upper Loup Loup Creek.

Summary for analysis for the 303(d) listings for DO

The Okanogan CD DO data is not suitable for the assessment of DO impairment. Of the listed tributaries, only upper Sinlahekin and lower Ninemile Creeks were monitored during the pH verification study:

- Sinlahekin Creek showed evidence of biological productivity which could not be unassociated from potential anthropogenic causes. Due to this, it is recommended to keep the creek on the 303(d) list. However, the DO saturation in the creek, given the warmer water temperature and elevation of the site is expected to be below the 9.5 mg/L criterion for the site.
- Ninemile Creek showed no evidence of biological productivity during the verification study. Both the pH and the DO were close to saturation levels throughout the 24-hour periods that were monitored. The DO in Ninemile was below the 9.5 mg/L DO criterion because the saturation levels were below 9.5 mg/L. This study recommends delisting both reaches on Ninemile Creek for DO impairment.

Upper Tonasket and Loup Loup Creeks do not have biological activity based on proxy of the pH data collected at lower reaches on those creeks for the verification study.

Recommendations for 303(d) listings for DO

- Sinlahekin Creek shows signs of biological productivity and it is not clear if this is due to natural or anthropogenic causes. Both DO listings on Sinlahekin Creek should remain on the 303(d) list for further investigation.
- DO listings for Ninemile, Loup Loup, and Tonasket Creeks should be delisted.

Appendix G. Glossary, acronyms, and abbreviations

Glossary

Anthropogenic: Human-caused.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Diel: Of, or pertaining to, a 24-hour period.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Exceedance: A water quality measurement that does not meet a specific set numeric limit (criterion) for a parameter, or is out of bounds of a specific set numeric range (criteria) for a parameter. A measurement above or below (depending on the parameter) the numeric range for a parameter is considered an exceedance (out of bounds).

Impairment: A detriment to the beneficial uses of a water body due to the water quality criteria for a parameter not being met due to unnatural causes.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Riparian: Relating to the banks along a natural course of water.

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and abbreviations

CD	Conservation District
CO_2	Carbon dioxide
DO	(See Glossary above)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
FMU	Freshwater Monitoring Unit (Dept of Ecology)
LLID	Longitude Latitude Identification
MQO	Measurement quality objective
QA	Quality assurance
QC	Quality control
RM	River mile
SOP	Standard Operating Procedure
TMDL	(See Glossary above)
USGS	U.S. Geological Survey

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft	feet
m	meter
mg	milligram
mg/L	milligrams per liter (parts per million)
mg/L/hr	milligrams per liter per hour
mL	milliliters
NTU	nephelometric turbidity units
s.u.	standard units
ug/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter
uS/cm	microsiemens per centimeter, a unit of conductivity