



DEPARTMENT OF  
**ECOLOGY**  
State of Washington

## **Quality Assurance Project Plan**

---

### **Lower White River pH and Nutrients Study**

October 2009

Publication No. 09-03-131

## Publication Information

This plan is available on the Department of Ecology's website at [www.ecy.wa.gov/biblio/0903131.html](http://www.ecy.wa.gov/biblio/0903131.html).

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at [www.ecy.wa.gov/eim/index.htm](http://www.ecy.wa.gov/eim/index.htm). Search User Study ID, NMat0002.

Ecology's Project Tracker Code for this study is 10-156.

Waterbody Number: WA-10-1040

## Author and Contact Information

Nuri Mathieu  
P.O. Box 47600  
Environmental Assessment Program  
Washington State Department of Ecology  
Olympia, WA 98504-7710

For more information contact: Carol Norsen, Communications Consultant  
Phone: 360-407-7486

Washington State Department of Ecology - [www.ecy.wa.gov/](http://www.ecy.wa.gov/)

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

*Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.*

*To ask about the availability of this document in a format for the visually impaired, call Carol Norsen at 360-407-7486.*

*Persons with hearing loss can call 711 for Washington Relay Service.*

*Persons with a speech disability can call 877- 833-6341.*

# Quality Assurance Project Plan

---

## Lower White River pH and Nutrients Study

October 2009

### Approved by:

Signature:

Cindy James, Client, Water Quality Program, SWRO

Date: September 2009

Signature:

Kim McKee, Client's Unit Supervisor, Water Quality Program, SWRO

Date: September 2009

Signature:

Garin Schrieve, Client's Section Manager, Water Quality Program, SWRO

Date: September 2009

Signature:

Nuri Mathieu, Author /Project Manager/EIM Data Engineer, WOS, EAP

Date: September 2009

Signature:

George Onwumere, Author's Unit Supervisor, WOS, EAP

Date: September 2009

Signature:

Robert F. Cusimano, Author's Section Manager, WOS, EAP

Date: September 2009

Signature:

Stuart Magoon, Director, Manchester Environmental Laboratory, EAP

Date: September 2009

Signature:

Bill Kammin, Ecology Quality Assurance Officer

Date: September 2009

Signatures are not available on the Internet version.

SWRO – Southwest Regional Office.

WOS – Western Operations Section.

EAP – Environmental Assessment Program.

EIM – Environmental Information Management system.

# Table of Contents

	<u>Page</u>
List of Figures and Tables.....	3
Abstract.....	4
Background.....	5
Overview.....	5
Study area.....	5
What causes high pH levels in the Lower White River? .....	6
What has been done in response to pH exceedances? .....	6
Project Description.....	7
Why is Ecology conducting a verification study? .....	7
Organization and Schedule .....	9
Laboratory Budget .....	11
Quality Objectives .....	12
Sampling Design (Experimental Design) .....	14
Periphyton nutrient analysis.....	16
Sampling Procedures .....	17
Measurement Procedures .....	18
Quality Control Procedures.....	19
Field .....	19
Laboratory.....	19
Data Management Procedures .....	19
Audits and Reports.....	20
Data Verification.....	20
Data Quality (Usability) Assessment.....	20
References.....	21
Appendix. Glossary, Acronyms, and Abbreviations .....	23

# List of Figures and Tables

Page

## Figures

Figure 1. Comparison of mean monthly flows at the USGS gage on the Lower White River at A St. (RM 6.3) for water years 2001, 2006, and 2007. ....	8
Figure 2. Map of Lower White River and sampling stations.....	15

## Tables

Table 1. Organization of project staff and responsibilities.....	9
Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports. ....	10
Table 3. Cost estimate for laboratory sample analysis. ....	11
Table 4. Measurement quality objectives for Hydrolab post deployment checks. ....	12
Table 5. Measurement quality objectives for field measurements and laboratory analysis. ....	13
Table 6. Station names, descriptions, and coordinates. ....	14
Table 7. Sampling schedule. ....	15
Table 8. Data collection schedule and activities.....	16
Table 9. Containers, preservation techniques, and holding times for sampled parameters. ....	17

## Abstract

The White River, located in the Puget Sound basin in western Washington, originates from several glaciers on Mt. Rainier. The river flows westerly until emptying into the Puyallup River near Sumner, Washington.

In September and October of 1990, Ecology measured pH levels that did not meet (exceeded) water quality standards in the Lower White River at river mile 4.9, 6.3, and 8.0. These measurements were taken during a Total Maximum Daily Load (TMDL) study conducted in the Puyallup River watershed. Subsequent monitoring, conducted from 1993-2001, documented continued exceedances of pH standards in the Lower White River.

Based on the pH exceedances, the White River was placed on Washington State's Section 303(d) list of impaired waterbodies. The federal Clean Water Act of 1972 requires the state to (1) develop a water quality improvement report or TMDL, and (2) implement activities in the plan to bring these waterbodies back into compliance with standards.

Interested parties have done additional data collection and analysis in support of a TMDL; however, a TMDL has not yet been finalized. Recent improvements in wastewater treatment will likely result in reduced nutrient loads. In addition, changes in river flows due to changes in the management of withdrawals may increase the nutrient loading capacity. This study will provide additional information about the Lower White River and the effects of improved wastewater treatment.

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. The primary goal of this study is to collect diurnal pH data at key locations along the Lower White River. After completion of the study, a final report describing the study results will be posted to the Internet.

# Background

## Overview

The White River, located in the Puget Sound basin in western Washington, originates from several glaciers on Mt. Rainier. The river flows westerly until emptying into the Puyallup River near Sumner, Washington (Erickson, 1999).

In September and October of 1990, Ecology measured pH levels that did not meet (exceeded) water quality standards in the Lower White River at river mile (RM) 4.9, 6.3, and 8.0. These measurements were taken during a Total Maximum Daily Load (TMDL) study conducted on the Puyallup River watershed (Pelletier, 1993). Subsequent monitoring, conducted from 1996-2003, documented continued exceedances of pH standards in the Lower White River (Erickson, 1999; Ecology, 2009; Stuart, 2002; Ebbert, 2003).

Based on the pH exceedances, the White river was placed on Washington State's 303(d) list of impaired waterbodies. The federal Clean Water Act of 1972 requires the state to (1) develop a water quality improvement report or TMDL and (2) implement activities in the plan to bring these waterbodies back into compliance with standards.

Interested parties have completed additional data collection and analysis in support of a TMDL; however, a TMDL has not yet been finalized. Recent improvements in wastewater treatment will likely result in reduced nutrient loads. In addition, changes in river flows due to changes in the management of withdrawals may increase the nutrient loading capacity. This study will provide additional information about the Lower White River and the effects of improved wastewater treatment.

## Study area

The White River drains a 494-square-mile basin with a total length of 68 miles. Mud Mountain Dam, around river mile (RM) 28, provides flood control for the river valley and affects flows in the river downstream.

A diversion at RM 24 removes a regulated amount of water which is temporarily stored in Lake Tapps and then returned to the White River at about RM 4.

Historically, the majority of the White River was diverted to Lake Tapps and used for hydroelectric power generation by Puget Sound Energy (PSE). The mainstem of the White River from the diversion to the return was referred to as the "bypass reach." This reach contained the minimum baseflow deemed necessary to serve as a fish bypass around the diversion, Lake Tapps, and the hydroelectric plant.

The Muckleshoot Indian Tribe owns and governs reservation land along the Lower White River within the study area. The White River flows through Muckleshoot land between RMs 16 and 9. Surface waters that flow into the reservation boundaries are considered waters of the state

upstream of the boundary and tribal waters downstream of the boundary. The opposite applies to waters flowing downstream out of tribal land.

In January 2004, PSE ceased hydropower operations. The majority of flow was then returned to the White River bypass reach, while diverting a much smaller amount of water to maintain water levels in Lake Tapps for recreation.

The Cascade Water Alliance recently purchased the water rights to the diversion from PSE. The Alliance and the Puyallup and Muckleshoot tribes reached an agreement outlining future management of the White River and Lake Tapps for protection of fishery resources, providing municipal water supply, and continuing recreational use of Lake Tapps.

The study area for this project extends from RM 25.1, just upstream of the Rainier School wastewater treatment plant (WWTP), to RM 4.9, downstream of the City of Auburn and about one mile upstream of the Lake Tapps return.

## **What causes high pH levels in the Lower White River?**

Excess nutrients in the White River promote benthic algal growth (periphyton) on rocks, or other debris, in the streambed. These algae remove dissolved inorganic carbon from the water column; dissolved inorganic carbon is needed for photosynthesis.

Carbon dioxide ( $\text{CO}_2$ ) hydrates in water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which then disassociates into a hydrogen ion ( $\text{H}^+$ ) and bicarbonate ( $\text{HCO}_3^-$ ). Thus, the more  $\text{CO}_2$  in the water, the more hydrogen ions in the water, and the lower the pH level. During daylight hours, algae consume dissolved  $\text{CO}_2$  in the water column for photosynthesis, causing the pH to increase.

In waters with excessive algal growth, inorganic carbon uptake can occur at a rate much faster than it is replenished by the atmosphere. This results in high pH levels that can be harmful to aquatic life.

## **What has been done in response to pH exceedances?**

In 1996, The Washington State Department of Ecology (Ecology) initiated an assimilative capacity study. The goal of the study was to identify the amount of nutrients that can be added to the White River without causing water quality standards to be violated. Ecology intended the study to be a first step in developing a TMDL for pH and nutrients in the lower White River (Erickson, 1999).

In 2000 and 2001, Derek Stuart, a graduate student at the University of Washington, conducted his thesis research on periphyton-induced pH spikes in the Lower White River (Stuart, 2002). The thesis study conducted surveys of flow, nutrient levels, and periphyton biomass along the Lower White River from RMs 27 to 6.3 with the idea that the data could be used to help develop a TMDL.



In the fall of 2001, the Muckleshoot Indian Tribe, U.S Environmental Protection Agency (EPA), and Ecology signed a Memorandum of Agreement (MOA) to develop a TMDL for pH on the Lower White River.

Subsequently, technical staff of the MOA parties developed two water quality models, one of pH and one of periphyton biomass, in the Lower White River. The models used the Stuart thesis data set and are the basis of the draft TMDL. The TMDL will set wasteload allocations for permitted discharges to the Lower White River.

In anticipation of potential wasteload allocations from the TMDL, Buckley and Enumclaw WWTPs upgraded their treatment facilities to reduce nutrient loading and control eutrophication in the White River.

## **Project Description**

### **Why is Ecology conducting a verification study?**

Since water year (WY) 2001, two major changes have occurred within the Lower White River. These changes raise the question of whether or not the draft TMDL models are able to accurately predict current conditions:

1. The flow regime has changed dramatically now that PSE is no longer diverting large amounts of water for power generation.
  - a. In WY 2001, the Lower White River system had low-flow, steady-state conditions in the fall and early winter, through January.
  - b. Compared to WY 2001, the system now has greater than triple the baseflow. The river is heavily influenced by large precipitation events where flows can spike by as much as an order of magnitude above WY 2001 levels (Figure 1), particularly from November to January. This suggests that the critical period for pH and eutrophication may have changed and may no longer extend into January.
2. The Buckley and Enumclaw WWTPs, the two major point sources within the area of concern, have upgraded their nutrient-removal capabilities within the last year.

In addition, Ecology's ambient monitoring program collected grab samples from 2004 to 2008 that suggest the Lower White River may currently be meeting the pH standards (Ecology, 2009). However, the data are not continuous, and pH was often not measured in the afternoon when peak pH values typically occur.

A monitoring study is now needed to provide additional information about the Lower White River and the effects of improved wastewater treatment. The primary goal of the study is to collect diurnal pH (using Hydrolabs deployed for 48-hour periods) at key locations along the river.

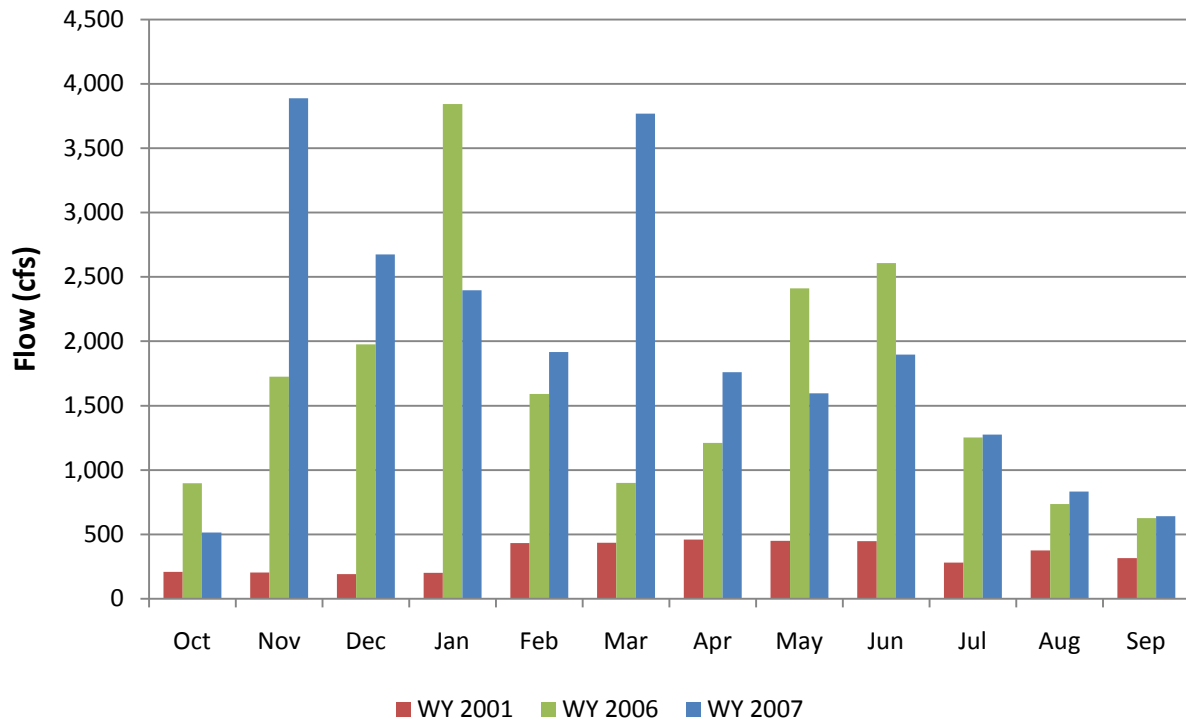


Figure 1. Comparison of mean monthly streamflows at the USGS gage on the Lower White River at A St. (RM 6.3) for water years 2001, 2006, and 2007.

## Organization and Schedule

The following people are involved in this project. All are employees of the Washington State Department of Ecology (Table 1).

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Cindy James Water Quality Program Southwest Regional Office Phone: (360) 407-6556	EAP Client	Clarifies scopes of the project, provides internal review of the QAPP, and approves the final QAPP.
Nuri Mathieu Directed Studies Unit Western Operations Section Phone: (360) 407-7359	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Trevor Swanson Directed Studies Unit Western Operations Section Phone: (360) 407-6685	Field Investigator	Assists with developing study design and sampling/ Hydrolab deployment logistics. Helps collect samples and record field information.
George Onwumere Directed Studies Unit Western Operations Section Phone: (360) 407-6730	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, tracks progress, approves the budget, and approves the final QAPP.
Robert F. Cusimano Directed Studies Unit Western Operations Section Phone: (360) 407-6596	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

EAP – Environmental Assessment Program.

QAPP – Quality Assurance Project Plan.

QA – Quality Assurance

EIM – Environmental Information Management system.

Table 2 provides the project schedule for completing the work. Table 7, under the *Sampling Design* section, provides a more detailed sampling schedule.

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	January 2010	Nuri Mathieu
Laboratory analyses completed	January 2010	
Environmental Information System (EIM) database		
EIM user study ID	NMat0002	
Product	Due date	Lead staff
EIM data loaded	June 30, 2010	Nuri Mathieu
EIM quality assurance	July 15, 2010	Markus Von Prause
EIM complete	July 31, 2010	Nuri Mathieu
Final report		
Author lead	Nuri Mathieu	
Schedule		
Draft due to supervisor	April 30, 2010	
Draft due to client/peer reviewer	May 15, 2010	
Draft due to external reviewer(s)	May 31, 2010	
Final (all reviews done) due to publications coordinator	June 30, 2010	
Final report due on web	July 31, 2010	

## Laboratory Budget

Table 3 displays the estimated laboratory budget and sample load. This is an estimate only. Costs include 50% discount for Manchester Environmental Laboratory.

The budget is based on 4 total events sampled. If there is a dry winter and sampling extends into January then the maximum budget for sampling during all 7 potential events is \$12,500.

Table 3. Cost estimate for laboratory sample analysis.

Parameter	\$/samples	No. of samples	Cost
<b>Nutrient Sampling</b>			
Turbidity	\$11	24	\$264
Total Suspended Solids(TSS)	\$11	24	\$264
Alkalinity	\$17	24	\$408
Chloride	\$13	24	\$312
Chlorophyll-a	\$55	24	\$1,320
Total Persulfate Nitrogen (TPN)	\$17	24	\$408
Ammonia (NH3)	\$13	24	\$312
Nitrate/Nitrite (NO2/NO3)	\$13	24	\$312
Orthophosphate (OP)	\$15	24	\$360
Total Phosphorus (TP)	\$18	24	\$432
Dissolved Organic Carbon (DOC)	\$35	24	\$840
Total Organic Carbon (TOC)	\$33	24	\$792
		Total	\$6,024
<b>Periphyton Surveys</b>			
Chlorophyll-a	\$55	84	\$4,620
TSS	\$11	49	\$539
Chlorophyll-a (method comparison)	\$55	24	\$1,320
		Total	\$6,479
		<b>Total</b>	<b>\$12,503</b>

## Quality Objectives

Field sampling procedures and laboratory analysis inherently have associated error. Measurement quality objectives state the allowable error for a project. Precision and bias are data quality criteria used to indicate conformance with measurement quality objectives.

- *Precision* is defined as the measure of variability in the results of replicate measurements due to random error. Random error is imparted by the variation in concentrations of samples from the environment as well as other introduced sources of variation (e.g., field and laboratory procedures). Precision for replicates will be expressed as percent relative standard deviation (%RSD).
- *Bias* is defined as the difference between the population mean and true value of the parameter being measured. Bias affecting measurement procedures can be inferred from the results of Quality Control procedures involving the use of blanks, check standards, and spiked samples. Bias in field measurements will be minimized by strictly following sampling and handling protocols, and will be assessed by submitting field blanks.

Hydrolabs will be calibrated before each run and post checked afterwards using conductivity/pH buffer solutions and the air saturation calibration method for dissolved oxygen. Table 4 contains the measurement quality objectives for post-check values.

Table 4. Measurement quality objectives for Hydrolab post deployment checks.

Parameter	Units	Accept	Qualify	Reject
pH	standard units	< or = $\pm 0.2$	> $\pm 0.2$ and < or = $\pm 0.5$	> $\pm 0.5$
Conductivity*	$\mu\text{S}/\text{cm}$	< or = $\pm 5\%$	> $\pm 5\%$ and < or = $\pm 15\%$	> $\pm 15\%$
Dissolved Oxygen**	% saturation	< or = $\pm 5\%$	> $\pm 5\%$ and < or = $\pm 10\%$	> $\pm 10\%$

\* Criteria expressed as a percentage of readings. For example, buffer = 100.2  $\mu\text{S}/\text{cm}$  and Hydrolab = 98.7  $\mu\text{S}/\text{cm}$ ;  $(100.2-98.7)/100.2 = 1.49\%$  variation, which would fall into the acceptable data criteria of less than 5%.

\*\*When Winkler data are available, they will be used to evaluate acceptability of data in lieu of % saturation criteria.

When possible, field staff will deploy Hydrolab sondes with a low-ionic LISREF (Beckman<sup>®</sup> Red Label Lazaran<sup>™</sup>) pH reference electrode. Field staff will calibrate pH meters with conventional buffers and then check probes against low-ionic strength buffers both before and after calibration.

Analytical methods, expected precision of sample replicates, and method reporting limits and/or resolution are presented in Table 5. The targets for analytical precision of laboratory analyses are based on historical performance by Manchester Environmental Laboratory (MEL) for environmental samples taken around the state by the Watershed Ecology Section (Mathieu, 2006). The reporting limits of the methods listed in the table are appropriate for the expected range of results and the required level of sensitivity to meet project objectives. MEL's measurement quality objectives and quality control procedures are documented in the MEL Lab Users Manual (MEL, 2008).

Table 5. Measurement quality objectives for field measurements and laboratory analysis.

Analysis	Method	Bias (% deviation from true value)	Precision (replicate median RSD)	Reporting Limits and Resolution
<b>Field Measurements</b>				
Water Temperature <sup>1</sup>	Hydrolab <sup>®</sup>	n/a	+/- 0.1° C	0.01° C
Specific Conductivity <sup>2</sup>	Hydrolab <sup>®</sup>	n/a	+/- 0.5%	0.1 umhos/cm
pH <sup>1</sup>	Hydrolab <sup>®</sup>	n/a	0.05 SU	1 to 14 SU
Dissolved Oxygen <sup>1</sup>	Hydrolab <sup>®</sup>	n/a	5% RSD	0.1 - 15 mg/L
Dissolved Oxygen <sup>1</sup>	Winkler Titration	n/a	+/- 0.1 mg/L	0.01 mg/L
<b>Laboratory Analyses</b>				
Alkalinity	SM 2320	n/a	10% RSD <sup>3</sup>	10 mg/L
Chloride	EPA 300.0	n/a	5% RSD <sup>3</sup>	0.1 mg/L
Chlorophyll-a	SM 10200H(3)	n/a	20% RSD <sup>3</sup>	0.05 ug/L
Total Suspended Solids	SM 2540D	n/a	15% RSD <sup>3</sup>	1 mg/L
Turbidity	SM 2130	n/a	15% RSD <sup>3</sup>	1 NTU
Dissolved Organic Carbon	EPA 415.1	10	10% RSD <sup>3</sup>	1 mg/L
Total Organic Carbon	EPA 415.1	10	10% RSD <sup>3</sup>	1 mg/L
Total Persulfate Nitrogen	SM 4500-NO <sub>3</sub> <sup>-</sup> B	10	10% RSD <sup>3</sup>	0.025 mg/L
Ammonia	SM 4500-NH <sub>3</sub> -H	5	10% RSD <sup>3</sup>	0.01 mg/L
Nitrate/Nitrite	4500-NO <sub>3</sub> <sup>-</sup> I	5	10% RSD <sup>3</sup>	0.01 mg/L
Orthophosphate	SM 4500-P G	5	10% RSD <sup>3</sup>	0.003 mg/L
Total Phosphorus	EPA 200.8	5	10% RSD <sup>3</sup>	0.001 mg/L

<sup>1</sup> As units of measurement, not percentages.

<sup>2</sup> As percentage of reading, not relative standard deviation (RSD).

<sup>3</sup> Replicate results with a mean of less than or equal to 5X the reporting limit will be evaluated separately.

EPA = U.S. Environmental Protection Agency.

SM = standard method.

## Sampling Design (Experimental Design)

The study design consists of three data collection components:

- Continuous Hydrolab deployments at all sites.
  - Measure pH, dissolved oxygen, conductivity, and temperature.
  - Record data in 15-minute intervals.
  - Deploy for 48 hours or more (per deployment).
- Periphyton sampling at all sites.
  - Scrub and rinse rocks for sample collection and analyze for chlorophyll-a and Ash-Free Dry Mass (AFDM).
  - Measure surface area of rock.
  - Estimate periphyton biomass at each site.
- Nutrient sampling at only 3 sites (Table 6).
  - Collect samples listed under *Laboratory Analysis* in Table 5.
  - Field staff will filter orthophosphate and dissolved organic carbon samples; lab staff will filter chlorophyll-a samples.

Ecology will conduct each field component monthly from September 2009 to January 2010 at six stations along the mainstem of the Lower White River (Table 6; Figure 2).

Table 6. Station names, descriptions, and coordinates.

Station Name	Location Description	Latitude °N	Longitude °W	Nutrients
10-WHT-25.1	Just upstream of Rainier School WWTP	47.16626	-121.99328	X
10-WHT-20.4	At 80 <sup>th</sup> and 274 <sup>th</sup> ; downstream of Enumclaw and Buckley	47.18772	-122.06889	X
10-WHT-16.2	PSE power line access road; just upstream of Muckleshoot Reservation	47.22499	-122.11278	--
10-WHT-8.0	Just upstream of Bowman Creek in Auburn	47.27487	-122.20855	--
10-WHT-6.3	At A St./railroad tracks in Auburn	47.26657	-122.22900	X
10-WHT-4.9	At 8 <sup>th</sup> St. in Sumner; downstream of Auburn	47.24997	-122.24408	--



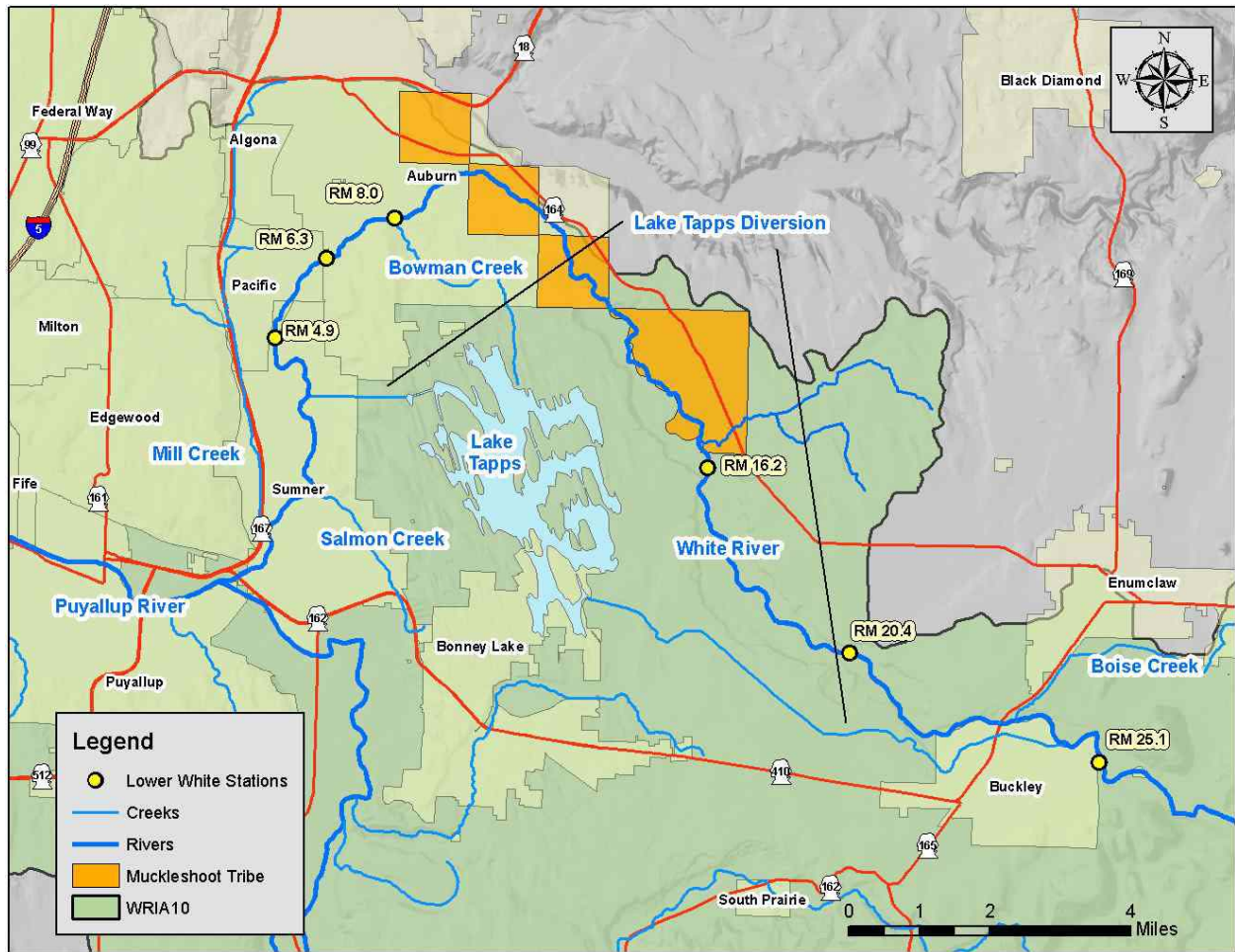


Figure 2. Map of Lower White River and sampling stations.

Table 7 contains a proposed schedule for sampling. Sample events will occur only in late November, December, and January if it is a dry year, flows stay at or return to near baseflow levels, and sites are accessible.

Table 7. Sampling schedule.

	Sept. 2009	Early Oct. 2009	Late Oct. 2009	Early Nov. 2009	Late Nov. 2009	Dec. 2009	Jan. 2010
# of events	1	1	1	1	1*	1*	1*

\*Potential sample event based on conditions.

For each sampling event, data collection will occur over the course of three days (Table 8). Ecology will collect Winkler dissolved oxygen samples and *in situ* Hydrolab measurements for each site at deployment, mid-deployment, and upon retrieval at all sites. *In situ* measurements will be taken using the same Hydrolab for all sites. This Hydrolab will be calibrated daily and used both as a Quality Assurance check on, and comparison between, the deployed probes. Field staff will download continuous data on the second day and assess probes for fouling, drift, or

failure. If any issues are identified, the Hydrolab will be cleaned and recalibrated, or replaced with a pre-calibrated backup Hydrolab.

Table 8. Data collection schedule and activities.

Field component	Day 1	Day 2	Day 3
Hydrolab deployments	<ul style="list-style-type: none"> <li>- Deploy Hydrolabs at all sites moving upstream.</li> <li>- Collect Winkler samples and <i>in situ</i> Hydrolab measurements moving downstream.</li> </ul>	<ul style="list-style-type: none"> <li>- Take <i>in situ</i> measurements using a freshly calibrated Hydrolab.</li> <li>- Collect Winkler samples.</li> <li>- Download continuous data.</li> </ul>	<ul style="list-style-type: none"> <li>- At each site: take <i>in situ</i> Hydrolab measurements, collect a Winkler sample, and then retrieve Hydrolab.</li> </ul>
Periphyton sampling	<ul style="list-style-type: none"> <li>- No activity.</li> </ul>	<ul style="list-style-type: none"> <li>- Collect duplicate periphyton samples at all sites.</li> <li>- Ship to MEL.</li> </ul>	<ul style="list-style-type: none"> <li>- MEL receives samples and begins analysis.</li> </ul>
Nutrient sampling	<ul style="list-style-type: none"> <li>- No activity.</li> </ul>	<ul style="list-style-type: none"> <li>- Collect nutrient samples at 3 sites.</li> <li>- Ship to MEL.</li> </ul>	<ul style="list-style-type: none"> <li>- MEL receives samples and begins analysis.</li> </ul>

## Periphyton nutrient analysis

A sub-set of periphyton samples will be analyzed for total carbon, nitrogen, and phosphorus content. Ecology plans to test the utility and data quality of these analyses for future use in TMDL studies. An addendum to this Quality Assurance Project Plan is forthcoming and will include project details.

## Sampling Procedures

Standard Ecology protocols will be used for sample collection, preservation, and shipping to Manchester Environmental Laboratory (MEL) (Joy, 2006; MEL, 2008; Ward, 2007). Chain-of-custody signatures will be required during sample transport. Table 8 contains containers, preservation methods, and holding times for each parameter.

Ecology will collect samples directly into pre-cleaned containers supplied by MEL. Samples will be stored in the dark, on ice, and shipped to MEL. Samples will be available at MEL for analysis within 24 hours of collection.

Table 9. Containers, preservation techniques, and holding times for sampled parameters.

Parameter	Sample Matrix	Container	Preservative	Holding Time
Alkalinity	Surface water, POTW effluent, & runoff	500 mL poly – no headspace	Cool to 0-6°C; Fill bottle <i>completely</i> ; Don't agitate sample	14 days
Chloride	Surface water, POTW effluent, & runoff	500 mL poly	Cool to 0-6°C	28 days
Chlorophyll-a	Surface water, POTW effluent, & runoff	500 mL amber poly	Cool to 0-6°C; store in the dark until filtration.	24 hours – before filtering; 28 day – after filtering
Total Suspended Solids	Surface water, POTW effluent, & runoff	1000 mL poly	Cool to 0-6°C	7 days
Turbidity	Surface water, POTW effluent, & runoff	500 mL poly	Cool to 0-6°C	48 hours
Ammonia	Surface water, POTW effluent, & runoff	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 0-6°C	28 days
Dissolved Organic Carbon	Surface water, POTW effluent, & runoff	60 mL poly with 0.45um pore size filters <sup>1</sup>	Filter in field with 0.45um pore size filter; 1:1 HCl to pH<2; Cool to 0-6°C	28 days
Nitrate/Nitrite	Surface water, POTW effluent, & runoff	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 0-6°C	28 days
Total Persulfate Nitrogen	Surface water, POTW effluent, & runoff	125 mL clear poly	H <sub>2</sub> SO <sub>4</sub> to pH<2; Cool to 0-6°C	28 days
Orthophosphate	Surface water, POTW effluent, & runoff	125 mL amber poly with 0.45um pore size filters <sup>2</sup>	Filter in field with 0.45um pore size filter; Cool to 0-6°C	48 hours
Total Phosphorus	Surface water, POTW effluent, & runoff	60 mL clear poly	1:1 HCl to pH<2; Cool to 0-6°C	28 days
Total Organic Carbon	Surface water, POTW effluent, & runoff	60 mL clear poly	1:1 HCl to pH<2; Cool to 0-6°C	28 days

<sup>1</sup> Whatman Puradisc™ 25pp, or equivalent, with a polypropylene media filter designed for aqueous and organic solutions containing high debris levels and for hard-to-filter solutions.

<sup>2</sup> Whatman GD/X 25mm, or equivalent, with a cellulose acetate filter membrane. A glass microfiber prefilter may be used for “hard to filter” orthophosphate samples.

Ecology's periphyton field sampling protocols are adapted from the revised USGS protocols (Moulton et al., 2002). Periphyton biomass samples will be collected by scraping material from a measured surface area on representative rocks. Three samples will be collected at each site. Periphyton biomass samples are collected for laboratory analysis of chlorophyll-a and ash-free dry weight. Samples will not be collected for species verification. Benthic area coverage by periphyton or macrophytes will be estimated for each site using a grid and random sampling technique. Notes on general periphyton and macrophyte types will be taken (e.g., filamentous, diatoms, reed canary grass, emergent weeds).

## Measurement Procedures

Ecology's Environmental Assessment Program field methods will be followed for the collection of dissolved oxygen, pH, temperature, and specific conductance and for the deployment of data recording equipment (Swanson, 2007). Field meter calibration will follow Environmental Assessment Program protocols under manufacturer's instructions (Swanson 2007). Criteria for accepting, qualifying, or rejecting field meter post-calibration results and subsequent field data are listed in Table 3. The project manager will determine the quality of the data and address usability in the final report. Calibration data, field measurement data, and other notes will be maintained on water resistant paper in field notebooks.

Hydrolab DataSonde® or MiniSonde® dissolved oxygen, pH, conductivity, and temperature probes will be cleaned, maintained, calibrated, and checked before and after each DataSonde® deployment to ensure proper functioning in the field. DataSondes® and their probes will be properly stored when not in use, following Hydrolab recommendations.

Specific conductivity is relatively low in the Lower White River with values typically below 100  $\mu\text{S}/\text{cm}$  (Ecology, 2009). When possible, field staff will deploy Hydrolab sondes with a low-ionic LISREF (Beckman® Red Label Lazaran™) pH reference electrode. The LISREF electrode is designed to reduce unstable potentials in the reference electrode junction caused by low-ionic strength waters.

Field staff will calibrate pH meters with conventional buffers and then check probes against low-ionic strength buffers both before and after calibration.

## Quality Control Procedures

Total variation from field sampling and analytical processes will be assessed by collecting and analyzing replicate samples. Sample precision will be assessed by collecting replicates for approximately 10-20% of samples in each survey. MEL routinely duplicates sample analyses in the laboratory to determine the presence of bias in analytical methods. The difference between field variability and laboratory variability is an estimate of the sample field variability.

### Field

Field sampling and measurements will follow quality control protocols described in Ecology's field sampling protocols (Joy, 2006; Swanson, 2007; Ward, 2007). If any of these quality control procedures are not met, the associated results will be qualified and used with caution, or not used at all.

### Laboratory

MEL will analyze all samples. MEL's measurement quality objectives and quality control procedures are documented in the MEL Quality Assurance Manual (MEL, 2006). MEL will follow standard quality control procedures (MEL, 2006).

## Data Management Procedures

Field measurement data will be entered into a field book with waterproof paper in the field and then entered into EXCEL<sup>®</sup> spreadsheets (Microsoft, 2007) as soon as practical after returning from the field. This database will be used for preliminary analysis and to create a table to upload data into Ecology's Environmental Information Management (EIM) System.

Sample result data received from MEL by Ecology's Laboratory Information Management System (LIMS) will be exported prior to entry into EIM and added to a cumulative spreadsheet for laboratory results. This spreadsheet will be used to informally review and analyze data during the course of the project.

An EIM user study (NMat0002) has been created for this study, and all monitoring data will be available via the internet after the project data have been validated. The URL address for this geospatial database is: [www.ecy.wa.gov/eim/](http://www.ecy.wa.gov/eim/). All data will be uploaded to EIM by the EIM data engineer after the data have been reviewed for quality assurance and finalized.

All spreadsheet files, paper field notes, and GIS products created as part of the data analysis and model building will be kept with the project data files.

## **Audits and Reports**

The project manager will submit a data summary report to the client for this project according to the project schedule, if necessary.

### **Data Verification**

Laboratory-generated data reduction, review, and reporting will follow the procedures outlined in the MEL Users Manual (MEL, 2008). Lab results will be checked for missing and/or improbable data. Variability in lab duplicates will be quantified using the procedures outlined in the Users Manual. Any estimated results will be qualified and their use restricted as appropriate. A standard case narrative of laboratory QA/Quality Control results will be sent to the project manager for each set of samples.

Field notebooks will be checked for missing or improbable measurements before leaving each site. The EXCEL<sup>®</sup> Workbook file containing field data will be labeled “DRAFT” until data verification and validity are completed. Data entry will be checked against the field notebook data for errors and omissions. Valid data will be moved to a separate file labeled “FINAL.”

Data received from LIMS will be checked for omissions against the “Request for Analysis” forms by the field lead. Data can be in EXCEL<sup>®</sup> spreadsheets (Microsoft, 2007) or downloaded tables from EIM. These tables and spreadsheets will be located in a file labeled “DRAFT” until data validity is completed. Field replicate sample results will be compared to quality objectives in Table 5. Data requiring additional qualifiers will be reviewed by the project manager.

After data validity and data entry tasks are completed, all field, laboratory, and flow data will be entered into a file labeled “FINAL,” and then into the EIM system. EIM data will be independently reviewed by another Environmental Assessment Program field assistant for errors at an initial 10% frequency. If significant entry errors are discovered, a more intensive review will be undertaken. At the end of the field collection phase of the study, the data will be compiled in a data summary.

### **Data Quality (Usability) Assessment**

The field lead will verify that all measurement and data quality objectives have been met for each monitoring station. If the objectives have not been met (such as percent RSD for sample replicates exceeds the measurement quality objectives or a Hydrolab was recording bad data), the project manager will decide how to qualify the data and how the data should be used in the analysis or whether the data should be rejected.



## References

- Ebbert, J.C., 2003. Water Temperature, Specific Conductance, pH, and Dissolved-Oxygen Concentrations in the Lower White River and the Puyallup River Estuary, Washington, August-October 2002. U.S. Geological Survey, Water-Resources Investigations Report 03-4177, Tacoma, WA.
- Ecology, 2009. Water quality monitoring station: 10C095 - White River @ R Street. Finalized Data. Washington State Department of Ecology, Olympia, WA. [www.ecy.wa.gov/apps/watersheds/riv/station.asp?sta=10C095](http://www.ecy.wa.gov/apps/watersheds/riv/station.asp?sta=10C095).
- Erickson, K., 1999. Review Draft: Assimilative Capacity Study for Nutrient Loading in the Lower White River. Washington State Department of Ecology, Olympia, WA. Publication No. 00-03-001. [www.ecy.wa.gov/biblio/0003001.html](http://www.ecy.wa.gov/biblio/0003001.html).
- Joy, J., 2006. Standard Operating Procedure for Grab Sampling – Fresh water, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html).
- Mathieu, N., 2006. Replicate Precision for 12 TMDL Studies and Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-044. [www.ecy.wa.gov/biblio/0603044.html](http://www.ecy.wa.gov/biblio/0603044.html).
- MEL, 2006. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.
- MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.
- Microsoft, 2007. Microsoft Office XP Professional, Version 10.0. Microsoft Corporation.
- Moulton II, S.R., Kennen, J.G., Goldstein, R.M., and J.A. Hambrook, 2002. Revised Protocols for Sampling Algal, Invertebrate, and Fish Communities as Part of the National Water-Quality Assessment Program. U.S. Geological Survey, Open-File Report 02-150, Reston, Virginia.
- Pelletier, G., 1993. Puyallup River Total Maximum Daily Load for Biochemical Oxygen Demand, Ammonia, and Residual Chlorine. Washington State Department of Ecology, Olympia, WA. Publication No. 96-326. [www.ecy.wa.gov/biblio/96326.html](http://www.ecy.wa.gov/biblio/96326.html).
- Stuart, D., 2002. A study of periphyton induced pH spikes on the White River, Washington. Master's thesis. Department of Civil and Environmental Engineering, University of Washington, Seattle.

Swanson, T., 2007. Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html).

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington Washington State Department of Ecology, Olympia, WA. [www.ecy.wa.gov/laws-rules/ecywac.html](http://www.ecy.wa.gov/laws-rules/ecywac.html).

Ward, W.J., 2007. Collection, Processing, and Analysis of Stream Samples, Version 1.3. Washington State Department of Ecology, Olympia, WA. SOP Number EAP034. [www.ecy.wa.gov/programs/eap/quality.html](http://www.ecy.wa.gov/programs/eap/quality.html).



## Appendix. Glossary, Acronyms, and Abbreviations

**Ambient:** Background (environmental). Away from point sources of contamination.

**Benthic:** Bottom-dwelling organisms.

**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.

**Dissolved oxygen:** A measure of the amount of oxygen dissolved in water.

**Diurnal:** Daytime only, as opposed to nocturnal or crepuscular.

**Eutrophication:** An increase in productivity resulting from nutrient loads from human activities such as fertilizer runoff and leaky septic systems.

**Grab sample:** A discrete sample from a single point in the water column.

**Nonpoint source:** Pollution that enters any waters of the state from any dispersed land-based or water-based activities. This includes, but is 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.

**Nutrient:** Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

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

**Periphyton:** Algae that grow on submerged rocks, plants, and debris.

**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 that clear more than 5 acres of land.

**Pollution:** Such 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 is 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.

**Total Maximum Daily Load (TMDL):** A water cleanup plan. A distribution of a substance in a waterbody designed to protect it from 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.

**Water year:** October 1 through September 30. For example, WY07 is October 1, 2006 through September 30, 2007.

**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.

## Acronyms and Abbreviations

Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GIS	Geographic Information System software
HCl	Hydrogen chloride
LIMS	Laboratory Information Management System
MEL	Manchester Environmental Laboratory
POTW	Publicly owned treatment works
PSE	Puget Sound Energy
QA	Quality assurance
RM	River mile
RSD	Relative standard deviation
SOP	Standard operating procedures
TMDL	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area
WWTP	Wastewater treatment plant

### *Units of Measurement*

°C	degrees centigrade
mg/L	milligrams per liter (parts per million)
NTU	nephelometric turbidity units
SU	standard units
umhos/cm	micromhos per centimeter
μS/cm	microsiemens per centimeter, a unit of conductivity