

Little Spokane River Watershed Dissolved Oxygen and pH Total Maximum Daily Load Study

Water Quality Study Design (Quality Assurance Project Plan)



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Authors: Joe Joy, phone 360-407-6486; Scott Tarbutton, phone 509-329-3453. Communication Consultant: phone 360-407-6834.

Washington State Department of Ecology - www.ecy.wa.gov/

- Headquarters, Olympia
 Northwest Regional Office, Bellevue
 425-649-7000
- Northwest Regional Office, Denevue 423-049-7000
 Southwest Regional Office, Olympia 360-407-6300
- o Southwest Regional Office, Olympia 500-407-6
- Central Regional Office, Yakima 509-575-2490
 Eastern Regional Office, Snakana 500-220-2400
- Eastern Regional Office, Spokane509-329-3400

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Cover photo: Ecology Ambient Site 55B100: Little Spokane River above Deadman Creek.

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Approved by:

Signature:	Date: July 2010
Karin Baldwin, Client, WQP, Eastern Regional Office	
Signature:	Date: July 2010
Dave Knight, Client's Unit Supervisor, WQP, Eastern Regional Office	
Signature:	Date: July 2010
Jim Bellatty, Client's Section Manager, WQP, Eastern Regional Office	
Signature:	Date: July 2010
Joe Joy, Author / Project Manager, EOS, EAP	
Signature:	Date: July 2010
Scott Tarbutton, Author / Principal Investigator, EOS, EAP	
Signature:	Date: July 2010
Dan Sherratt, EIM Data Engineer, EOS, EAP	
Signature:	Date: July 2010
Gary Arnold, Author's Section Manager, EOS, EAP	
Signature:	Date: August 2010
Stuart Magoon, Director, Manchester Environmental Laboratory	
Signature:	Date: August 2010
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.

WQP - Water Quality Program

EOS – Eastern Operations Section

EAP - Environmental Assessment Program

EIM - Environmental Information Management system

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Abstract

Several areas of the Little Spokane River are on Washington State's list of polluted waters (303(d) list) and require a cleanup plan, or total maximum daily load (TMDL). While TMDL assessments are in progress for temperature, bacteria, and turbidity, additional data are needed to address dissolved oxygen and pH 303(d) listings in the Little Spokane River watershed.

The Washington Water Research Center and Washington State University collected data from 2004 to 2006. They identified several key factors contributing to dissolved oxygen and pH criteria violations in the watershed, but data were not sufficient for a complete TMDL analysis.

The Washington State Department of Ecology (Ecology) will conduct two intensive synoptic surveys in the summer of 2010 to address the potential sources of nutrients and other factors affecting dissolved oxygen and pH in the Little Spokane River watershed. Ecology will enter the data from the surveys into its Environmental Information Management online database and complete a data summary report. The technical TMDL analysis will be completed in a Water Quality Improvement Report later when staff and resources are available.

Each study conducted by 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. After Ecology completes the data summary report, it will be posted to the Intranet.

What is a Total Maximum Daily Load (TMDL)?

Federal Clean Water Act requirements

The Clean Water Act established a process to identify and clean up polluted waters. The Act requires each state to have its own water quality standards designed to protect, restore, and preserve water quality. Water quality standards consist of (1) designated uses for protection, such as cold water biota and drinking water supply, and (2) criteria, usually numeric criteria, to achieve those uses.

The Water Quality Assessment and the 303(d) List

Every two years, states are required to prepare a list of waterbodies that do not meet water quality standards. This list is called the Clean Water Act 303(d) list. In Washington State, this list is part of the Water Quality Assessment (WQA) process. Ecology conducted its most recent water quality assessment in 2008.

To develop the WQA, the Washington State Department of Ecology (Ecology) compiles its own water quality data along with data from local, state, and federal governments, tribes, industries, and citizen monitoring groups. All data in this WQA are reviewed to ensure that they were collected using appropriate scientific methods before they are used to develop the assessment. The list of waters that do not meet standards [the 303(d) list] is the Category 5 part of the larger assessment.

- Category 1 Meets standards for parameter(s) for which it has been tested.
- Category 2 Waters of concern.
- Category 3 Waters with no data or insufficient data available.
- Category 4 Polluted waters that do not require a TMDL because they:
 - 4a. Have an approved TMDL being implemented.
 - 4b. Have a pollution control program in place that should solve the problem.
 - 4c. Are impaired by a non-pollutant such as low water flow, dams, or culverts.
- Category 5 Polluted waters that require a TMDL the 303(d) list.

Further information is available at Ecology's <u>Water Quality Assessment website</u>.

The Clean Water Act requires that a total maximum daily load (TMDL) be developed for each of the waterbodies on the 303(d) list. A TMDL is numerical value representing the highest pollutant load a surface waterbody can receive and still meet water quality standards. Any amount of pollution over the TMDL level needs to be reduced or eliminated to achieve clean water.

TMDL process overview

Ecology uses the 303(d) list to prioritize and initiate TMDL studies across the state. The TMDL study identifies pollution problems in the watershed and specifies how much pollution needs to be reduced or eliminated to achieve clean water. Ecology, with the assistance of local governments, tribes, agencies, and the community, then develops a strategy to control and reduce pollution sources and a monitoring plan to assess effectiveness of the water quality improvement activities. Together, the study and implementation strategy comprise the *Water Quality Improvement Report* (WQIR).

Once the U.S. Environmental Protection Agency (EPA) approves the WQIR, a *Water Quality Implementation Plan* (WQIP) is published within one year. The WQIP identifies specific tasks, responsible parties, and timelines for reducing or eliminating pollution sources and achieving clean water.

Who should participate in this TMDL?

Nonpoint source pollutant load targets will likely be set in this TMDL. Because nonpoint pollution comes from diffuse sources, all land owners in upstream watershed areas have the potential to affect downstream water quality. Therefore, all land owners in the watershed must use the appropriate best management practices to reduce impacts to water quality. The area that will be subject to the TMDL is shown in Figure 1.

Similarly, all point source dischargers in the watershed must also comply with the TMDL. Little Spokane Fish Hatchery effluent and treated groundwater from the Colbert Landfill will be evaluated, as will stormwater from various dischargers.

Ecology and the Spokane County Conservation District (CD) will be working with the Little Spokane River Watershed Committee, Pend Oreille CD, Spokane County, the City of Spokane, Washington Department of Fish and Wildlife, Washington State Department of Transportation, and others to recommend and implement actions that improve water quality in the watershed.

Clean Water Act requirements in a TMDL

Loading capacity, allocations, seasonal variation, margin of safety, and reserve capacity

A waterbody's *loading capacity* is the amount of a given pollutant that a waterbody can receive and still meet water quality standards. The loading capacity provides a reference for calculating the amount of pollution reduction needed to bring a waterbody into compliance with the standards.



Figure 1. Study area (hatched area) for the Little Spokane River Dissolved Oxygen and pH Total Maximum Daily Load study.

The portion of the receiving water's loading capacity assigned to a particular source is a *wasteload* or *load* allocation. If the pollutant comes from a discrete (point) source subject to a National Pollutant Discharge Elimination System (NPDES) permit, such as a municipal or industrial facility's discharge pipe, that facility's share of the loading capacity is called a *wasteload allocation*. If the pollutant comes from diffuse (nonpoint) sources not subject to an NPDES permit, such as general urban, residential, or farm runoff, the cumulative share is called a *load allocation*.

The TMDL must also consider *seasonal variations*, and include a *margin of safety* that takes into account any lack of knowledge about the causes of the water quality problem or its loading capacity. A *reserve capacity* for future pollutant sources is sometimes included as well.

Therefore, a TMDL is the sum of the wasteload and load allocations, any margin of safety, and any reserve capacity. The TMDL must be equal to or less than the loading capacity.

Surrogate measures

To provide more meaningful and measurable pollutant loading targets, this TMDL will incorporate *surrogate measures* other than daily loads of dissolved oxygen (DO) and pH. EPA regulations [40 CFR 130.2(i)] allow other appropriate measures in a TMDL. See the Glossary section of this document for more information.

Potential surrogate measures for use in this TMDL are discussed below. The ultimate need for, and the selection of, a surrogate measure for use in setting allocations depends on how well the proposed surrogate measure directly affects DO and pH values and how well it matches the selected implementation strategy.

Other than natural conditions, Little Spokane River watershed DO and pH criteria violations are directly affected by other pollutants or poor stream conditions. Excessive nutrients and biological oxygen demand (BOD), high water temperatures, poor channel conditions from erosion and sedimentation, and low streamflows are possible contributors to DO and pH problems. Nitrogen and phosphorus are likely limiting nutrients that may be the best surrogate TMDL allocation parameters.

Nutrients such as nitrogen, phosphorus, and carbon (as BOD) do not have numeric state or federal standards for running freshwater systems such as the Little Spokane River. Nutrient concentrations that cause DO and pH problems can be very site-specific and measureable as loads, e.g., pounds per day or kilograms per day. These loads can be allocated to point and nonpoint sources. Heat loads previously allocated from the temperature TMDL will also be used. Recommendations for channel improvements and water conservation will be made. Together these measures should reduce the frequency and intensity of DO and pH criteria violations.

Why is Ecology Conducting a TMDL Study in This Watershed?

Background

Total maximum daily load assessments of the Little Spokane River watershed have been in progress since 2003 (McBride and Butler, 2003) to address 303(d) listings for temperature, bacteria, turbidity, DO, and pH. Ecology gave a contract to Washington State University (WSU) and the Washington Water Research Center (WWRC) in 2004 to conduct a comprehensive water quality study addressing the first three parameters and to characterize DO, pH, and nutrients, especially phosphorus (Cichosz et.al., 2005; Barber et al., 2007). Nitrogen, phosphorus, and carbon are essential nutrients for aquatic biomass growth. Excessive biomass can cause problems with DO and pH concentrations.

Ecology has been using the results of the WSU/WWRC study and previous studies by the Spokane County CD and the Pend Oreille CD to complete TMDL assessments for fecal coliform, turbidity, and temperature (Joy and Jones, in progress).

The 2008 303(d) assessment has increased to 12 DO and 10 pH listings in the Little Spokane River watershed (Table 1). The newer listings are based on 2004-06 data (Barber et al., 2007) and recent comparisons to more stringent DO criteria that are a result of the Little Spokane River being a tributary to Lake Spokane. Lake Spokane must meet criteria that supports core summer salmonid habitat. Therefore, as of 2008 the Little Spokane River and its tributaries must comply with the same criteria.

Based on a preliminary review of water quality data collected by WSU/WWRC (Barber et al., 2007) and others (POCD, 1999; SCCD, 2003), several more reaches in the watershed may not meet the more stringent DO criterion. Diel monitoring and measurements taken by WSU/WWRC documented DO concentrations below the 9.5 mg/L criterion at three Little Spokane River mainstem sites that are not currently listed (Painted Rock, above Deadman Creek, and at Deer Park-Milan Road). One or more DO concentrations below the new criterion were also recorded at the mouths of Dry, Deer, Deadman, Dragoon, and Otter Creeks. Ecology's ambient monitoring database (Ecology, 2010a) and past surveys (POCD, 1999; SCCD, 2003) also indicate many other mainstem and tributary sites in the watershed have not always met the 9.5 mg/L criterion in the past, especially during the summer months.

Previous grab sampling and limited diel data also suggest pH violations may be more geographically prevalent and more frequent than is apparent in the 303(d) listings. DO and pH criteria often do not meet criteria when high temperatures, elevated nutrients, and adequate habitat for periphyton (algae growing on things in the water) and macrophytes (large aquatic plants) are present. Many reaches of the Little Spokane River and its tributaries have these conditions during the low-flow season.

Although WSU/WWRC and the conservation districts have collected samples that expanded DO and pH 303(d) listings in the watershed, the quantity of data was not adequate to complete a TMDL. A data set of more detailed nutrient, temperature, DO, and pH measurements are needed to determine their interactions and identify potential sources. As a requirement of the TMDL, the data must also help determine background conditions not caused by human sources. The Little Spokane River watershed has several areas where natural wetlands, groundwater inputs, and open lakes can greatly influence DO and pH values.

Waterbody	Parameter	Medium	Listing ID	Township	Range	Section
	DO	Water	42597	26N	42E	05
Little Spekene Diver	DO	Water	47875*	30N	45E	08
	pН	Water	50434	27N	43E	33
	pН	Water	50436	29N	43E	35
Dartford Creek	pН	Water	50416	26N	43E	06
	DO	Water	41981	26N	43E	01
Deadman Crack	рН	Water	50410	26N	43E	01
Deadman Creek	рН	Water	50411	27N	44E	33
	pН	Water	11388	27N	43E	33
Little Deep Creek	pН	Water	50401	27N	43E	33
Peone Creek	DO	Water	47055	26N	44E	08
Dragoon Crock	DO	Water	47094	29N	42E	34
Dragoon Creek	pН	Water	50397	28N	43E	33
Unnamed Spring at Kaiser	DO	Water	42359	26N	43E	03
Dry Creek	pН	Water	50373	29N	44E	30
	pН	Water	50379	29N	43E	15
West Dranch Little Onekens	DO	Water	47073	29N	43E	15
west Branch Little Spokane	DO	Water	47862	30N	43E	32
	DO	Water	47863	31N	43E	34
Beaver Creek	DO	Water	47869	30N	43E	18
Buck Creek	DO	Water	47872	30N	43E	06
Moon Creek	DO	Water	47861	30N	44E	08

Table 1. Study area waterbodies on the 2008 303(d) list for parameters.

* Bold indicates waterbody listing IDs not addressed in this TMDL study.

Study area

The Little Spokane River consists of a West Branch and East Branch that converge upstream of Milan (Figure 1). The river then continues down to Lake Spokane. The focus of the TMDL will be the Little Spokane River mainstem from below Eloika Lake on the West Branch and Chain Lake on the East Branch, through the area between Milan and Dartford, to the mouth where it enters Lake Spokane (Figure 1). The study area lies entirely within the Spokane Valley Outwash Plain Ecoregion.

Several 303(d) listings in the upper West and East Branches will not be assessed (Table 1). Evaluation of the water quality of lakes and wetlands upstream of the affected reaches require too many resources than are available at this time. To adequately address sources of DO and pH criteria violations other than naturally caused by the presence of these upstream physical features will require a specialized set of studies.

Major tributaries in the Little Spokane River watershed also have DO and pH 303(d) listings. Additional data during the critical low-flow season from the lower free-flowing reaches of Dragoon, Deadman, and Little Deep Creeks will be collected to address the listings. However from a review of the data, the listings in the upper reaches of these tributaries are based on data taken when either flows are nearly depleted or during a completely different time of year. Neither condition can be addressed in the TMDL without changes in current water quality policies on intermittent streams and another study during the winter months.

Impairments addressed by this TMDL

The main beneficial use to be protected by this TMDL is aquatic life in the Little Spokane River watershed and the Spokane River. The Little Spokane River and its tributaries have not been identified as having special populations of salmon to protect (Table 602 of WAC 173-201A-602) However, several salmonid communities are present, and other aquatic life and critical aquatic habitats have been described (McLellan, 2003a; 2003b; 2005; Spokane County, 2008).

The surviving native species most sensitive to water quantity and quality are redband trout and mountain whitefish. Sections of the Little Spokane River mainstem and Little Deep, Deadman, Dragoon, and Dartford Creeks have remnant populations of redband trout (Western Native Trout Initiative, 2007; McLellan, 2005). Based on the 2001 and 2002 surveys conducted by the Washington Department of Fish & Wildlife (WDFW), mountain whitefish are currently present in the Little Spokane River drainage encompassing Bear Creek, Dry Creek, Little Spokane River, Otter Creek, West Branch Little Spokane River, Wethey Creek, Horseshoe Lake, and Chain Lakes (McLellan, 2003a; 2003b).

Instream flow studies related to these two species are being conducted as part of the watershed planning assessment work (Spokane County, 2008). The watershed website summary goes on to say:

On-going Washington Department of Fish & Wildlife (WDFW) studies have identified additional fish species in the Little Spokane River system: eastern brook trout, bluegill,

bridgelip sucker, grass pickerel, green sunfish, northern pikeminnow, largemouth bass, longnose and speckled dace, pumpkinseed, sculpin, sucker, tench, yellow bullhead, and yellow perch.

However, there is no major effort to re-establish anadromous (sea-run) salmon or steelhead in the Little Spokane River watershed because of downstream barriers in the Spokane River system. But improving water quality conditions would be a necessary step for enhancing and protecting all aquatic communities, including cold water fisheries. Proper levels of DO and pH are essential for healthy fish and macroinvertebrate populations.

To meet standards for the parameters in Table 1, loading of the following pollutants will need to be characterized and appropriately decreased:

- Nitrogen and phosphorus.
- Carbonaceous biochemical oxygen demand.
- Temperature (heat).

How will the results of this study be used?

A TMDL study identifies how much pollution needs to be reduced or eliminated to achieve clean water. This is done by assessing the situation and recommending practices to reduce pollution, and by establishing limits for facilities that have permits. Since the study may also identify the main sources or source areas of pollution, Ecology and local partners use these results to figure out where to focus water quality improvement activities. Also the study sometimes suggests areas for follow-up sampling to further pinpoint sources for cleanup.

The DO and pH TMDL is an extension of Ecology's water quality cleanup work in the Little Spokane River watershed and Spokane River basin. Ecology will be collecting additional water quality data to make a quantitative assessment of sources and possible solutions to the DO and pH problems. Data from previous Little Spokane River TMDLs for temperature and suspended sediment also will be used in the assessment.

The water quality of the Little Spokane River watershed is important to the aquatic community and the people along the Little Spokane River and Lake Spokane. Aquatic life in the Little Spokane River watershed requires protection from poor water quality conditions, and understanding the source of poor conditions is necessary. Residents would enjoy aesthetic and recreational benefits from improved water quality in the river. With this information, better decisions can be made by the Little Spokane River Watershed Committee for implementation activities and by local and regional agencies for resource management.

Water quality work in the Spokane River basin is ongoing. The potential role of phosphorus, ammonia nitrogen, and BOD in DO and pH problems in the basin also has importance for Lake Spokane. Phosphorus, ammonia, and BOD load allocations for the Little Spokane River have been recommended to improve water quality in Lake Spokane. Results from this study will be compared to those recommendations. The comparisons will allow better management decisions.

Water Quality Standards and Numeric Targets

Dissolved oxygen

Aquatic organisms are very sensitive to reductions in the level of DO in the water. The health of fish and other aquatic species depends on maintaining an adequate supply of oxygen dissolved in the water. Oxygen levels affect growth rates, swimming ability, susceptibility to disease, and the relative ability to endure other environmental stressors and pollutants. While direct mortality due to inadequate oxygen can occur, Washington State designed the criteria to maintain conditions that support healthy populations of fish and other aquatic life.

Oxygen levels can fluctuate over the day and night in response to changes in climatic conditions as well as the respiratory requirements of aquatic plants and algae. Since the health of aquatic species is tied predominantly to the pattern of daily minimum oxygen concentrations, the criterion is based on the lowest 1-day minimum oxygen concentrations that occur in a waterbody.

In the Washington State water quality standards, freshwater aquatic life use categories are described using key species (salmonid versus warm-water species) and life-stage conditions (spawning versus rearing). Minimum concentrations of DO are used as criteria to protect different categories of aquatic communities, some of which are specified for individual rivers, lakes, and streams.

The Little Spokane River watershed has not been designated for protection of any special population of fish. However, since the Little Spokane River is a tributary to Lake Spokane which has a core summer salmonid habitat designation, it must comply with the criteria of the lake [WAC 173-201A-600(1)(a)(iii)]. The DO criterion for core summer salmon protection criteria states [WAC 173-201A-200(1)(d)]:

The one-day minimum dissolved oxygen concentration shall not fall below 9.5 mg/L more than once every ten years on average. When DO is lower than the criterion (or are within 0.2 mg/L of the criterion) due to natural conditions, then cumulative human-caused activities will not decrease the dissolved oxygen more than 0.2 mg/L.

The criterion above is used to maintain conditions where a waterbody is naturally capable of providing full support for its designated aquatic life uses. The standards recognize, however, that not all waters are naturally capable of staying above the fully protective DO criteria. When a waterbody is naturally lower in oxygen than the criteria, the state provides an additional allowance for further depression of oxygen conditions due to human activities. In this case, the combined effects of all human activities must not cause more than a 0.2 mg/l decrease below that naturally lower (inferior) oxygen condition.

The DO criterion may be quite restrictive for the Little Spokane River, especially during summer low-flows in July and August. Data are necessary to define or estimate DO conditions in the Little Spokane River that would seasonally occur without impacts from anthropogenic sources. For example, naturally low DO concentrations in groundwater are known to affect specific reaches of the watershed. Also, temperature and barometric pressure conditions can result in DO concentrations at 100% saturation that are below 9.5 mg/L. However, the role of nutrients and eutrophication in creating DO concentrations out of compliance during critical summer conditions is likely occurring in open reaches of the mainstem and tributaries as well.

While the numeric criteria generally apply throughout a waterbody, the criteria are not intended to apply to discretely anomalous areas such as in shallow stagnant eddy pools where natural features unrelated to human influences are the cause of not meeting the criteria. For this reason, the standards direct that one take measurements from well-mixed portions of rivers and streams.

рΗ

The pH of natural waters is a measure of acid-base equilibrium achieved by the various dissolved compounds, salts, and gases. pH is an important factor in the chemical and biological systems of natural waters. pH both directly and indirectly affects the ability of waters to have healthy populations of fish and other aquatic species. Changes in pH affect the degree of dissociation of weak acids or bases. This effect is important because the toxicity of many compounds is affected by the degree of dissociation.

While some compounds (e.g., cyanide) increase in toxicity at lower pH, others (e.g., ammonia) increase in toxicity at higher pH. While there is no definite pH range within which aquatic life is unharmed and outside which it is damaged, there is a gradual deterioration as the pH values are further removed from the normal range. However, at the extremes of pH lethal conditions can develop. For example, extremely low pH values (<5.0) may liberate sufficient carbon dioxide from bicarbonate in the water to be directly lethal to fish.

The state established pH criteria in the Washington State water quality standards primarily to protect aquatic life. The criteria also serve to protect waters as a source for domestic water supply. Water supplies with either extreme pH or that experience significant changes of pH even within otherwise acceptable ranges are more difficult and costly to treat for domestic water purposes. pH also directly affects the longevity of water collection and treatment systems, and low pH waters may cause compounds of human health concern to be released from the metal pipes of the distribution system.

In the state's water quality standards, two pH criteria are established to protect six different categories of aquatic communities. Since the Little Spokane River watershed has not been designated with a special category but does need to comply with core summer salmonid protection, the pH criterion is [WAC 173-201A-200(1)(g)]:

pH must be kept within the range of 6.5 to 8.5, with a human-caused variation within the above range of less than 0.2 units.

The criteria above are used to maintain conditions where a waterbody is naturally capable of providing full support for its designated aquatic life uses. The standards recognize, however, that not all waters are naturally capable of staying within the fully protective pH criteria. When a waterbody is naturally lower or higher than the criteria, this natural pH level becomes the local criteria. However, the state does not provide an additional allowance for further changes due to

human activities. Only when the pH is within the criteria range can the combined effects of all human activities cause not more than a 0.2 units change.

Nutrients

Eutrophication is a condition for a lake or stream where plant growth and lower water quality are associated with a high dissolved nutrient input. It can be a natural process that takes hundreds of years as lakes become wetlands and rivers fill valleys with sediment to become slow and marshy. Plants are stimulated by light, nutrients, low streamflows that create shallow depths, and elevated temperatures. Human activity can reduce shade along streams, add nutrients, withdraw water, and increase temperatures. When human-caused acceleration of the plant stimulation is present from nutrient inputs and other changes, it's called *cultural eutrophication*.

Cultural eutrophication probably affects periphyton (algae that grow on submerged rocks, plants, and debris) and macrophyte (large aquatic plants) growth in the Little Spokane River watershed during the summer low-flow period. Some observed local DO and pH criteria violations are probably associated with the excessive aquatic plant growth. Some portions of the creek channel become choked with aquatic weeds, emergent grasses, filamentous algae, and periphyton in the summer. Besides negatively affecting habitat and aesthetics, the excessive plant growth can also cause oxygen supersaturation during the day through photosynthesis, as well as oxygen deficits at night from respiration. The pH values over the day can swing beyond safe levels for fish and macroinvertebrates.

Nutrients such as nitrogen and phosphorus do not have numeric state or federal standards for running freshwater systems such as the Little Spokane River and its tributaries. In this TMDL, nutrients may be key pollutants for DO and pH criteria violations. So they are called *surrogate measures*. Nutrient concentrations that cause these problems can be very site-specific.

More recent EPA ecoregional nutrient guidelines suggest a more region-specific approach (EPA, 2000). Regions of similar geology, climate, soils, and vegetation should have similar background concentrations of nutrients. The EPA ecoregions are broken into different levels.

Five Level IV ecoregions (EPA, 2000) from the same Northern Rockies Level III Ecoregion (15) aggregate ecoregion subdivide the Little Spokane River watershed:

- Okanogan-Colville Xeric Valleys and Foothills (15r).
- Spokane Valley Outwash Plain (15s).
- Inland Maritime Foothills and Valleys (15u).
- Western Selkirk Maritime Forest (15w).
- Granitic Selkirk Mountains (15y).

The mainstem Little Spokane River and most of the watershed is in the Spokane Valley Outwash Plain Ecoregion. Only the higher elevation areas around the edges of the watershed are within the other four ecoregions.

The ecoregions suggest that there may be distinctive characteristics in soils and vegetation that could be important for evaluating pollutant loading and transport. Not enough data have been collected at Level IV, but samples combined from state and federal agencies at Level III are available to estimate a reference condition (Table 2). The reference concentrations are based on the median of four seasonal 25th percentile values of all data reported across the ecoregion. EPA (2000) suggests the 25th percentile is a starting reference concentration until local governments and entities can analyze samples from designated reference streams.

Table 2. EPA Level III ecoregion reference concentrations relevant to the Little Spokane River (EPA, 2000).

	Northern Rockies Ecoregion 15							
Parameter	Annual 25 th percentile	Fall 25 th percentile	Spring 25 th percentile	Summer 25 th percentile	Winter 25 th percentile			
Total Phosphorus (mg/L)	0.0078	0.007 (148)	0.010 (147)	0.008 (150)	0.0075 (109)			
Nitrate + Nitrite Nitrogen (mg/L)	0.020	0.010 (138)	0.020 (125)	0.010 (133)	0.040 (99)			
Turbidity (NTU)	0.78	0.6 (70)	1.63 (72)	0.90 (74)	0.65 (55)			

Number of samples used in statistical analysis in parentheses.

However, research has not been performed to evaluate the effect of the reference phosphorus and nitrogen concentrations on resident aquatic communities. For example, work has not been done for checking if reference concentrations support all beneficial uses and maintain water quality criteria such as DO and pH.

Watershed Description

Geographic setting

The Little Spokane River basin consists of a 700-square mile drainage area that includes regions located in north-central Spokane County, south Pend Oreille County, and southeast Stevens County in northeast Washington, as well as Bonner County in the state of Idaho (Figure 1). The Little Spokane River is a tributary to Lake Spokane (Long Lake), an impoundment of the Spokane River. The Pend Oreille River basin lies to the northeast and the Colville River basin lies to the northwest. The Little Spokane River watershed has been designated as Water Resource Inventory Area 55 (WRIA 55).

The Little Spokane River watershed is a broad basin surrounded by the Okanogan foothills to the west and the Selkirk bedrock highlands to the east. Elevations range from 1,553 feet above sea level near the mouth of the watershed to 5,878 feet atop Mt. Spokane. The western edge of the basin is formed by Scoop Mountain at an elevation of 3,998 feet west of Dragoon Creek. To the north, the West Branch Little Spokane River tributaries form on Boyer Mountain at an elevation of 5,256 feet (Figure 1).

Climate

The basin climate ranges from semiarid to sub-humid, with precipitation increasing northerly and easterly with altitude. In the lower part of the Little Spokane River valley, the precipitation is usually less than 20 inches per year, whereas in the higher northern and eastern parts of the basin, it gradually increases to 44 inches per year.

Table 3 shows the precipitation information measured at weather reporting stations at Deer Park, Mt. Spokane Summit, Newport, and the Spokane Weather Bureau at the Airport (WRCC, 2009). In addition to spatial variations, Table 3 indicates that there are considerable temporal variations in precipitation amounts.

Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
Deer Park	2.67	1.76	2.00	1.91	1.86	1.70	1.00	1.10	0.97	1.19	2.95	3.64	22.76
Mt. Spokane Summit	5.34	3.69	6.09	3.35	3.56	3.12	1.68	2.07	2.94	2.71	3.80	5.67	44.01
Newport	3.05	2.62	2.24	1.93	2.26	1.99	1.36	1.16	1.12	1.79	3.54	3.89	26.95
Spokane Airport	1.81	1.57	1.52	1.31	1.53	1.22	0.75	0.69	0.73	1.13	2.25	2.20	16.70

Table 3. Average monthly precipitation (inches), 1971-2000.

Air temperatures tend to be warmer in the summer and colder in winter from southwest to northeast (Table 4). A more complete description of the climate is presented in the WSU/WWRC Quality Assurance Project Plan (Cichosz et al., 2005).

Station Name		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Door Park 2E	Max	31.6	39.1	46.6	57.7	68.3	74.9	85.0	82.9	73.5	59.1	41.9	33.9
Deel Faik 2E	Mean	23.8	30.1	36.0	44.7	53.7	60.0	66.7	64.9	56.6	45.2	34.3	27.1
Mt Spokopo	Max	23.1	27.6	30.3	38.2	49.0	57.4	66.5	66.0	56.4	43.1	32.5	26.4
Mit. Spokane	Mean	18.1	22.8	24.8	31.7	41.9	49.3	57.8	57.5	48.7	37.0	27.5	21.6
Nowport	Max	31.6	38.6	48.4	59.5	69.2	75.8	85.2	84.4	73.9	58.4	40.8	33.2
Newport	Mean	24.7	29.8	37.1	45.3	53.6	59.9	65.8	64.4	56.2	45.4	34.0	27.4
Spokane Airport	Max	32.9	39.1	48.2	58.3	67.1	74.3	83.9	82.7	72.5	59.3	43.0	34.8
	Mean	27.2	32.1	39.4	47.4	55.4	62.2	69.8	68.6	59.5	48.5	36.5	29.6

Table 4. Average mean and maximum air temperature (degrees F) at selected stations.

With high mountains on the north and east of the Little Spokane River basin, there exists a large amount of surface water available on an annual basin-wide basis. However, the temporal variations in precipitation previously discussed produce large fluctuations in monthly runoff volumes. Precipitation in the high mountains, largely in the form of snowfall during the winter, produces high spring runoff when it is combined with spring rainfall. The tributary streams, having steep slopes in the headwaters, rapidly empty the surface runoff and suffer low summer flows, causing seasonal problems related to water temperature.

Little Spokane River sub-watersheds

The watershed can be naturally divided into the four major sub-watersheds:

- Upper Little Spokane River, the East Branch Little Spokane River, and tributaries above the confluence with the West Branch Little Spokane River.
- West Branch Little Spokane River from the confluence below Eloika Lake to Diamond Lake.
- Middle Little Spokane River and tributaries from the confluence of the two branches to Dartford.
- Lower Little Spokane River below Dartford to the mouth at Lake Spokane (Long Lake).

The mainstem of the two upper branches have several associated lakes and wetlands. The largest lakes are in the West Branch sub-watershed and include Eloika, Sacheen, Horseshoe, and Diamond. These are linked by sections of the West Branch or Moon Creek. Chain Lake, an enlargement of the Little Spokane River, is a similar feature in the eastern branch. The area is forested and is sparsely populated except for residences around the lakes. A rough comparison of available streamflow records indicates the Upper and West Branch sub-watersheds contribute 40% - 50% of the annual streamflow through the Middle sub-watershed to the U.S. Geological Survey (USGS) gage at Dartford.

The major tributaries are located in the Middle sub-watershed: Dragoon, Deer, Deadman, and Little Deep Creeks. Tributaries in the Middle watershed contribute approximately 30% - 40% of the annual Little Spokane River streamflow above the Dartford gage. The middle Little Spokane River flows through an area that has more agricultural land uses up the tributaries and more densely placed residences along the banks of the river. Dairies and larger livestock operations are located in the Dragoon Creek and Deadman Creek sub-watersheds. Deer Park along Dragoon Creek and Mead along Deadman Creek are the largest incorporated areas in the Little Spokane River watershed outside of Spokane.

The Lower sub-watershed is on the urban fringe of Spokane and is beginning to see more residential and commercial development activity. The riparian area of the mainstem Little Spokane River is somewhat protected here because of major wetlands and springs associated with the high groundwater input from the Hillyard Trough and Little Spokane Arm of the Spokane Valley-Rathdrum Prairie (SVRP) aquifer. The groundwater input accounts for more than 56% of the Little Spokane River outflow to Lake Spokane during the low-flow periods of July, August, and September. Most of the lower reaches have been set aside as part of Riverside State Park and the Little Spokane Fish Hatchery. Development is growing on the uplands draining to the river and tributaries.

Groundwater

Groundwater is important throughout the watershed as a domestic drinking water supply and as a source of high-quality water in the lower watershed. Groundwater from the SVRP aquifer Hillyard Trough and Little Spokane Arm is an important feature of the Little Spokane River below Dartford. The Deer Park, Green Bluff, Peone Prairie, Orchard Prairie, and Five Mile Prairie aquifers provide considerably less water, but are nevertheless important locally. Descriptions of these aquifers are provided in Cichosz et al. (2005).

The majority of natural groundwater discharge in the watershed occurs as baseflow to the Little Spokane River. In low-flow periods (especially August and September), discharge volumes at the Dartford gage average approximately 150 cfs and consist primarily of groundwater inflows (Chung, 1975). During summer drought periods, the entire discharge in the mainstem of the river is contributed by groundwater baseflow. The mainstem of the Little Spokane River upstream of the confluence with the West Branch Little Spokane River is groundwater flow (Chung, 1975). The discharge record for the Little Spokane River at Scotia also suggests that most of the water is derived from groundwater rather than surface runoff (SCCD, 2003).

The significance of groundwater input to the lower Little Spokane River watershed below Dartford can be seen in Figure 2. The two USGS gage stations, 12431000 and 12431500, are only 7.5 miles apart with no significant tributary input. The substantial increase in streamflow every month is due primarily to springs and groundwater discharge from the SVRP aquifer. On average, approximately 240 cfs – 250 cfs of groundwater inflow enters this short reach.



Figure 2. Comparison of flow between Little Spokane River at Dartford and near Dartford gaging stations for 12-year overlapping period of record through water year 2005 (Barber et al., 2007).

Surface water

Three USGS gages are currently in operation: 12431000 – Little Spokane River at Dartford; 12431500 – Little Spokane River near Dartford; and 12427000 Little Spokane River at Elk. The first two are located in the two lower sections of the Little Spokane River. The Little Spokane River at Elk is located in the Upper Little Spokane River sub-watershed and was reactivated in October 2008. Only recently has the West Branch sub-watershed been gaged. The Spokane County CD established gages in 2007 at the following locations:

- West Branch below Eloika Lake at Eloika Lake Road.
- West Branch at Fan Lake Road.
- West Branch at Harworth Road.

The Little Spokane River at Elk was in operation from 1948-1971 and was located upstream of the West Branch confluence at river mile (RM) 37.5. It represented a drainage area of 115 square miles. The Little Spokane River at Dartford is located at RM 11.4 and has a drainage area of 665 square miles. The Little Spokane River near Dartford is located at RM 3.9 and has a drainage are of 698 square miles.

Streamflows in the Little Spokane River have declined since the 1950s. However, flows vary considerably on an annual and seasonal basis. Streamflow declines are the result of increased water use as well as lower than average precipitation (Ecology, 1995).

Potential pollutant sources

Residents and businesses in small towns in the watershed use individual on-site septic tanks. Deer Park, the community at Diamond Lake, and Mountainside Middle School have wastewater treatment plants (WWTPs) that do not directly discharge to waterways (Table 5). Several sand and gravel operations and dairies are permitted or registered in the Middle and Upper subwatersheds. The Spokane Fish Hatchery at Griffith Springs discharges raceway water and other effluents to the lower reaches of the Little Spokane River (Figure 1). Groundwater is pumped from wells around the former Colbert Landfill, stripped of volatile organics, and discharged to the Little Spokane River.

Permit Number	Permit Holder	Receiving Water	Permit Type	
WAD980514541	Colbert Landfill	Little Spokane River	Remediation	
ST0008016D	Deer Park WWTP	To Ground		
ST0008029D	Diamond Lake WWTP	To Ground	Municipal	
ST0008111A	Mountainside Middle School	To Ground		
WAG507065C	WDOT Denison-Chattaroy			
WAG507022C	Spokane County PWD Dalton			
WAG507008C	Toners Excavating		Sand & Gravel General Permit	
WAG507095C	WDOT PS-C-313 Elk			
WAG507067C	Central Premix Concrete Elk			
WAG507027C	Spokane Rock Products Elk			
WAG137007D	WDFW Spokane Fish Hatchery	Little Spokane River	Upland Fin Fish General Permit	
		Little Spokane River		
WAR046506	Spokane County	Deadman Creek		
		Little Deep Creek		
WAR046505	City of Spokane	Little Spokane River	Stormwater	
		Little Spokane River		
WAR04000A	WDOT	Deadman Creek		
		Little Deep Creek		
9160	Kimebert Farm	No Discharge		
4204	Darilane Farms	No Discharge		
9191	Bettydon Jersey Farm	No Discharge		
9536	Reiters Holstein Dairy LLC	No Discharge	Dairy or Livestock Register	
6004	Schmidt Dairy	No Discharge		
9120	Dunrenton Ranch LLC	No Discharge		
4244	Hutchinson Dairy	No Discharge		

Table 5. Wastewater, stormwater and livestock facilities with permits in the Little Spokane River watershed.

WWTP = Wastewater treatment plant.

PWD = Public Works Department.

WDOT = Washington State Department of Transportation.

LLC = Limited Liability Corporation.

WDFW = Washington Department of Fish & Wildlife.

Christian (2003) estimated the Little Spokane River and its tributaries have lost 56% - 93% of their historical riparian vegetation. Residential and commercial uses, roads, railroads, crop fields, and pastures have replaced natural vegetation. Bank and field erosion, reduced shade, fertilizers, right-of-way chemicals, stormwater runoff, water withdrawals, and livestock associated with uses in the riparian area potentially negatively influence DO and pH in the Little Spokane River and its tributaries.

The Little Spokane River watershed becomes more urbanized as it approaches the City of Spokane. Spokane and surrounding suburbs in Spokane County have stormwater treatment systems, and the city and county have municipal stormwater permits (Table 5). Even residential and urbanized areas distant from the Little Spokane River require protection from stormwater effects (Figure 3). The Washington State Department of Transportation (WDOT) also is required to manage stormwater, along within Spokane County, under its municipal stormwater permit (Table 5).



Figure 3. An example of stormwater treatment methods used in the urbanizing areas of Little Spokane River (Spokane County, 2009b).

Historical Data Review

Dissolved oxygen results

The majority of instantaneous DO measurements taken during the 1998-99 (POCD, 1999) and 2004-06 (Barber et al., 2007) studies were greater than 9.5 mg/L at all sites through most of the year. In both studies, instantaneous DO concentrations below 9.5 mg/L only occurred at a majority of sites during July and August surveys. A few sites had DO concentrations below the criterion from May through October. Higher water temperatures and low discharge volumes (with accompanying low reaeration) appear to have an effect on depressing DO concentrations in some areas. Earlier studies on Dragoon Creek (Ross, unpublished; Lundgren, 1998) and Deadman Creek (SCCD, 2003) had similar findings.

Localized groundwater inflows may contribute to low DO concentrations at some sites. DO at the mouth of the Little Spokane River is probably influenced by groundwater that depresses concentrations below 9.5 mg/L from May through October almost every year since monitoring began in the 1970s (Ecology, 2010a). Base flow conditions in some tributaries also appear to be groundwater influenced and are characterized with low DO concentrations.

Apparent declining DO concentration and percent DO saturation trends based on monthly instantaneous measurements at the mouth of Little Spokane River (55B070) are probably associated with a change in sampling time (Figure 4). DO concentrations dropped when Ecology changed the usual time of sampling from afternoon to morning in October 2000 to April 2007 (Ecology, 2010a). No statistically significant trends were detected for DO and percent saturation collected within this period. A drop in DO during the growing season (May – October) would be expected if routine sampling were switched from afternoon to morning.

Diel monitoring was conducted in September 2005 at five sites in the watershed (Barber et al., 2007). DO concentrations below the 9.5 mg/L criterion were documented at all three Little Spokane River mainstem sites (the mouth, above Deadman Creek, and at Deer Park-Milan Road). DO concentrations below 8 mg/L were also recorded at the West Branch Little Spokane River below Eloika Lake. All of the DO concentrations recorded from Dragoon Creek at Crescent Road were greater than 10 mg/L at that time.



Figure 4. Trend analysis of monthly percent dissolved oxygen (DO) saturation measurements collected from the mouth of the Little Spokane River (55B070).

The period when measurements were taken in the early morning rather than the afternoon is shown, probably influencing the apparent declining trend.

pH results

The instantaneous pH measurements taken at sites in the Little Spokane River watershed do not show a strong seasonal pH pattern of criteria violations. Instead, the TMDL survey (Barber et al., 2007) and earlier surveys (POCD, 1999; Ecology, 2010a; SCCD, 2003) reported pH below 6.5 and above 8.5 in all seasons.

Diel pH data have been collected at six sites. Peak pH readings at Deadman Creek, the Little Spokane River at Deer-Milan Road, and Little Spokane River above Deadman Creek in September 2005 were greater than 8.5 (Barber et al., 2007). The pH readings at Dragoon Creek, the West Branch Little Spokane River below Eloika Lake, and the Little Spokane River at the mouth were all within criteria.

Based on the collection of datasets, Deadman Creek and its tributary, Little Deep Creek, have potential pH problems, exceeding maximum and minimum criteria. Dragoon Creek and the Little Spokane River between Deer-Milan Road and Deadman Creek also have multiple pH measurements beyond criteria during the March to October growing season. Because violations

occur outside of the growing season, the role of nutrients and resultant biomass increases on pH is not apparent in upper Deadman Creek.

Nutrient results

Nutrient concentrations in the Little Spokane River watershed are of concern to the watershed and to Lake Spokane. Nonpoint and point sources of nutrients are present in the watershed. Phosphorus and ammonia load allocations have been recommended for the Little Spokane River to prevent algal growth and DO losses in Lake Spokane (Ecology, 2010b). Nitrate concentrations in the Spokane Valley Rathdrum Prairie Aquifer are also of concern as an indicator of surface pollution contaminating the aquifer. Groundwater nutrient concentrations may affect water quality in the lower Little Spokane River, especially during the low-flow season.

The soluble reactive phosphorus (SRP) at Ecology's long-term monitoring site at the mouth of the Little Spokane River (55B070) showed no significant trend since low-level analyses were available in the mid-1990s (Figure 5a). For the same period, data indicated a significant upward trend in nitrate/nitrite concentrations (Figure 5b). Nitrate/nitrite in March through June drove the upward trend; no trend was found for July through October when groundwater inflow dominates the station.

Elevated concentrations of nitrates have been reported in Dragoon Creek (Hallock, 1996; Ross, unpublished), as well as Deadman and Little Deep Creeks (SCCD, 2003). Until recently, less concern has been raised within the watershed about phosphorus concentrations. Phosphorus has become more of a concern since the Little Spokane River was identified as a source of phosphorus to Lake Spokane.

During the 2004-06 surveys, the total inorganic nitrogen (TIN) concentration in the Little Spokane River rose steadily downstream while the total phosphorus concentration peaked around Deadman Creek (Figure 6). The lowest levels of total phosphorus and inorganic nitrogen during the 2004-06 surveys generally occurred at sites in the West Branch sub-watershed. Inorganic nitrogen concentrations dropped to undetectable levels during the March to October growing season in the West Branch.

In 2004-06, ammonia nitrogen was somewhat elevated at times in Dragoon Creek, Deadman Creek, and West Branch, but no concentration was over 1 mg/L to pose an aquatic toxicity threat (Barber et al., 2007).





Figure 5. Soluble reactive phosphorus (SRP) and nitrate/nitrite (NO2+NO3-N) concentration trends for monthly samples collected by Ecology at the mouth of the Little Spokane River, October 1994 to September 2009.



Figure 6. Median total phosphorus (TP) and total inorganic nitrogen (TIN) concentrations from samples collected over 16 months (All) and or only during March through September (GS) at mainstem sites in the Little Spokane River, 2004-06.

The paucity of SRP data in the watershed makes evaluations of eutrophication potential difficult. Inorganic nitrogen to SRP ratios (nitrogen:phosphorus) are commonly used to determine a limiting nutrient. Some nitrogen:phosphorus ratio calculations are available for Ecology sites and from Ecology studies in the Dragoon Creek watershed. TIN to SRP ratios at the mouth of the Little Spokane River show nitrogen is rarely limiting (Figure 7). Most ratios calculated from monthly water samples at the site are far above the 5 to 20 ratio level that would indicate a phosphorus-limiting condition. Figure 8 shows nitrogen may be limiting part of the year in the headwaters of the Little Spokane River at Scotia and in the middle reaches at Chattaroy.

Although nitrogen:phosphorus ratios may indicate whether nitrogen or phosphorus limit the amount of biomass growth, the data from various studies suggests ample nutrients are available at most sites in the watershed to support excessive biomass growth. Figure 8 shows how nitrate and total phosphorus concentrations at the mouth of the Little Spokane River compare to recommended ecoregion reference levels from EPA (EPA, 2000). Although total phosphorus analyses have become more accurate over the period of record, the concentrations of both nitrate and total phosphorus are greater than estimated reference conditions most of the year.



Figure 7. Ratios of total inorganic nitrogen (TIN) to soluble reactive phosphorus (SRP) at three sites on the Little Spokane River (LSR) based on Ecology monthly monitoring samples (Ecology, 2010a).



Figure 8. Nitrate-nitrogen and total phosphorus concentrations at the mouth of the Little Spokane River compared to EPA ecoregion reference concentrations.

Goals and Objectives

Goals

The primary project goals are to:

- 1. Provide a best estimate of the pollutant loading contributing to the DO and pH violations of Washington State water quality standards in the Little Spokane River and some of its tributaries.
- 2. Propose wasteload and load allocations throughout the watershed that will allow water quality standards to be met.

A secondary goal is to evaluate how any phosphorus and nitrogen allocations within the Little Spokane River meet the Lake Spokane DO TMDL phosphorus load allocations established for the Little Spokane River.

Objectives

The two goals will be accomplished by (1) conducting a technical analysis for DO and pH TMDLs in the Little Spokane River and some of its tributaries, and (2) re-evaluating a seasonal phosphorus loading analysis of the Little Spokane River in light of proposed allocations.

This Quality Assurance Project Plan outlines the field and analytical tasks necessary to achieve the objectives:

- Evaluate existing nutrient and diurnal DO and pH data for the 2008 303(d) listed and contributing areas from the mainstem Little Spokane River below Chain Lake to the mouth and also in the lower reaches of Dragoon, Deadman, Dartford, and Little Deep Creeks.
- Conduct two synoptic water quality surveys during the low-flow season (July August) to fill known data gaps.
- Enter data in Ecology's EIM system and organize into spreadsheets or a database.
- Write a detailed data summary report and TMDL water quality implementation report.

The data need to be collected in a manner useful for the QUAL2K computer model and other analytical tools for TMDL development. Therefore, temperature, discharge measurements, and physical characteristics of the creek channels will be needed as well.

Study Design

Overview

A preliminary review has determined previous studies conducted over the past ten years are not sufficient to complete a DO and pH TMDL for the Little Spokane River. Additional sampling is planned because recent TMDL analyses and field surveys have provided much, but not quite enough, of what is required for a TMDL. The remaining data collection and analyses are designed to provide diel and spatial DO, pH, and nutrient data needed during the critical low-flow season when water quality standards are least likely to be met. Geographically, the sampling has been limited to those areas where DO and pH criteria violations are most likely influenced by human-caused sources rather than natural causes.

Two intensive synoptic surveys are planned for the 2010 summer low-flow season during the weeks of July 26 and August 23. A synoptic survey is an intense effort of water quality data collection, often over a consecutive series of days. Sampling usually begins at sites in the uppermost limit of the study area and progresses downstream, periodically sampling and measuring changes in water quality characteristics of a block of water as it flows to the end of the study area. Past Little Spokane River watershed data have shown summer low-flow to be the most likely period when DO and pH values do not meet water quality criteria.

Because both branches of the upper Little Spokane River watershed run through one or more lakes and large wetlands, the upstream study area boundary was set as the mainstem Little Spokane River below the last of these impoundments, i.e., below Eloika and Chain Lakes (Figure 10). Temperature and chemical/biological dynamics within the lakes are complex and influence inter-lake reaches of the Little Spokane River. Characterizing any more specific causes of DO and pH variability, other than those caused by the physical presence of the upstream lake or wetland, would be beyond the resources of this project.

Once the additional data are obtained, an evaluation of historical and recent water quality can be completed. Human-caused sources of nutrients, temperature, and channel conditions can be compared to natural sources contributing to DO and pH criteria violations. Implementation measures can be recommended to meet pollutant allocations and load capacities.

Modeling and analysis framework

The analyses completed by WSU/WWRC (Barber et al., 2007) and by others (Ecology, 2010a; SCCD, 2003; POCD, 1999) have provided some elements of the DO and pH TMDL assessment. Nutrient load estimates from major tributaries into the Little Spokane River, and loads from the Little Spokane River to Lake Spokane, can be calculated using multiple regression model (Cohn, 2002) and ratio estimator techniques (Dolan et al., 1981). A QUAL2Kw model (Chapra and Pelletier, 2003) for the Little Spokane mainstem with point inputs from major tributaries has been developed for the previous temperature TMDL assessment (Joy and Jones, in progress; Barber et al., 2007).

Independent nutrient loading calculations using multiple regression and ratio estimator methods will be used at multiple sites to check order of magnitude agreement. The strategy worked well for checking suspended sediment loads used in the Little Spokane River turbidity TMDL (Joy and Jones, in progress).

The QUAL2Kw model framework is described in more detail in Appendix B. Modifications to the model require additional data to simulate the following:

- Biological functions.
- Nutrient cycling (nitrogen, phosphorus, and carbon).
- Diel and longitudinal DO and pH changes.

The QUAL2Kw model and other mathematical analyses will be developed to simulate observed seasonal, annual, and daily critical conditions. Model time-steps will be appropriate for the data collected and simulated. Critical conditions for QUAL2K simulations of DO and pH are characterized by a period of low streamflow and high water temperatures (July – September) but require hourly time steps. Nutrient loading will be calculated at a daily time-step where daily streamflow is available. Otherwise, monthly or seasonal loads will be calculated.

The QUAL2Kw model requires data for calibrations of longitudinal changes and diurnal ranges during the summer low-flow critical season. These data must be accurate to definitively characterize DO and pH water quality criteria that address daily extremes. The model requires averaged reach-specific data for physical channel, biomass, and water chemistry.

The QUAL2Kw model scenarios will include:

- Current conditions.
- Current conditions with reduced nutrient loads from sources capable of implementing best management practices or pollutant source-reduction measures.
- Reduced nutrient loads with temperature reductions in place from riparian shade improvements recommended by the temperature TMDL.

Comparison of the model outputs from these scenarios should provide a way to estimate the DO and pH loading capacity in various Little Spokane River and tributary reaches and to help recommend allocations.

Estimated nutrient loads at the mouth of the Little Spokane River under the various scenarios will be compared to the Spokane River and Lake Spokane DO allocations (Ecology, 2010b). Seasonal load estimates outside of the low-flow period will not be as reliable because the QUAL2Kw model has limited usefulness under dynamic streamflow conditions. Literature research will be used to estimate load reductions from the low-flow period to the rest of the year.

Synoptic surveys

For the 2010 synoptic surveys, field teams will measure water quality parameters and collect grab samples twice-a-day (morning and afternoon) at several sites along the mainstem Little Spokane River (Table 6). Several tributaries and the two point sources, Colbert Landfill treated leachate and the Little Spokane Fish Hatchery, will also be sampled (Figure 9).

Different sections of the river will be sampled each day over three or four days, roughly following the time of travel of a block of water from below Eloika Lake on the West Branch and Chain Lake on the East Branch down the mainstem to the confluence with Lake Spokane. The following is a tentative sampling schedule:

- Day 1: Upper Branches to Riverway Road at RM 25.4.
- Day 2: East Chattaroy Road at RM 23.1 to North Little Spokane Drive at RM 13.5.
- Day 3: North Dartford Drive at RM 10.8 to mouth at Highway 291 at RM 1.1.

	Location	RM	Latitude	Longitude	Past Site ID
	West Branch at Eloika outlet	WB 3.1	48.007068 N	-117.362659 W	LSRTMDL-23
Y 1	Camden bridge	39.5	48.040639 N	-117.243799 W	Near LS-2
	Elk bridge	37.1	48.016665 N	-117.276935 W	
	Dry Creek at Milan-Elk Road	34.6	47.986494 N	-117.295168 W	LSRTMDL-15
	Otter Creek at Elk to Hwy Rd	33.5	48.017483 N	-117.313351 W	LSRTMDL-18/LS-3
D	East Eloika Road	33.2	47.985013 N	-117.324777 W	
	Deer Park - Milan Road	31.8	47.969564 N	-117.333930 W	LSRTMDL-2/LS-4
	Bear Creek	27.8	47.951482 N	-117.360213 W	LSRTMDL-4
	Riverway Road	25.4	47.903826 N	-117.343799 W	
	East Chattaroy Road	23.1	47.889446 N	-117.355235 W	55B200
	Deer Creek at Hwy 2	23	47.888205 N	-117.354683 W	LSRTMDL-10
7	Dragoon Creek at Crescent Rd	21.3	47.875054 N	-117.372813 W	LSRTMDL-13
	Colbert Landfill outfall	19.8	47.862141 N	-117.360500 W	
D	Buckeye bridge	18	47.842539 N	-117.374677 W	
	East Colbert Road	16	47.823696 N	-117.373964 W	
	North Little Spokane Drive	13.5	47.798054 N	-117.382497 W	LSRTMDL-3/55B100
	Deadman Creek	13.1	47.795626 N	-117.380818 W	LSRTMDL-8
	North Dartford Drive	10.82	47.783368 N	-117.415605 W	LS-6/55B082
3	Dartford Creek at Hazard Rd	10.81	47.784358 N	-117.417264 W	LSRTMDL-7
λ	Waikiki Springs	9.4	47.774912 N	-117.421972 W	
V	West Waikiki Road	7.5	47.769751 N	-117.453781 W	55B080
D	Griffith Springs outfall	6.9	47.766577 N	-117.459786 W	
	Rutter Parkway	3.9	47.780833 N	-117.495999 W	LSRTMDL-21/55B075
	Highway 291	1.1	47.783274 N	-117.529822 W	LSRTMDL-26/55B070

Table 6. Synoptic survey sites tentatively identified in the Little Spokane River watershed.



Figure 9. Sites tentatively selected for the 2010 synoptic surveys on the Little Spokane River.

While grab samples are collected, continuous monitoring of diel DO, pH, and temperature changes will take place at selected sites. Continuous DO, pH, temperature, and conductivity data will be collected at two sites over the course of the survey using Hydrolab[®] multi-probe data recorders. Additional multi-probe meters will be deployed for 48 hours at two additional sites and then transferred to two other sites for the following 48 hours.

In addition to continuous and grab water quality data, other data will be collected as resources permit. Periphyton samples will be collected at four sites for chlorophyll-a and ash-free, dry- weight analyses that will help estimate primary productivity. Representative sites will be chosen during the field reconnaissance trip. If resources and time allow, riparian shade and other channel metrics may be checked against data previously collected by WSU and others (Barber et al., 2007; SCCD, 2003; Christian, 2003; Canwell, 2003).

The lowest reaches of Dragoon, Deadman, and Little Deep Creeks are free-flowing during the summer low-flow season. Groundwater input restores flows depleted through the middle reaches (SCCD, 2003). The low-flow volumes in Deer, Otter, Dry, and Dartford Creeks are more tenuous. The tentative selection of creek sites includes:

- Otter Creek at Elk to Hwy Road and at North Valley Road.
- Dry Creek at Milan-Elk Road and at North Dunn Road.
- Deer Creek at Hwy 2 and at North Elk Chattaroy Road.
- Dragoon Creek at Crescent Road and at Chattaroy Road.
- Deadman Creek at Shady Slope Road and at Peone Park (or Spokane County CD private owner?).
- Little Deep Creek at Shady Slope and Spokane County CD private owner (Bi-State project site?).
- Dartford Creek at Hazard Road and private owner up North Dartford Drive.

Reconnaissance visits to potential sites on the latter creeks will determine if they should be included in the synoptic surveys.

Upstream tributary sites have not yet been identified but will be selected before the synoptic surveys are conducted. Diel monitoring and nutrient sampling of these upstream tributary sites will be conducted either during the synoptic surveys schedule or on a different day, depending on staff and resources. Little Deep and Deadman Creek upstream sites may be established at former Spokane County CD sites (2003) or coincide with work proposed for the Bi-State Nonpoint Group for monitoring the Eaglewood neighborhood (HDR, 2010). Sites near the head of the groundwater return area and at the mouth of each creek will be sampled for the same parameters as the synoptic surveys. Diel monitoring of DO, pH, temperature, and conductivity will be conducted at an appropriate site in the affected reach.

Additional data collection

USGS, Spokane County CD, and Whitworth University currently operate the following streamflow gages:

- USGS: 12427000 Little Spokane River at Elk.
 - USGS: 12431000 Little Spokane River at Dartford.
- USGS: 12431500 Little Spokane River near Dartford.
- Spokane County CD: Little Spokane River at Deer Park-Milan Rd, Riverside.
- Spokane County CD: West Branch Little Spokane River below Eloika Lake.
- Spokane County CD: Dragoon Creek at Crescent Road near Chattaroy.
- Spokane County CD: Deadman Creek at Little Spokane River Drive near Mead.
- Whitworth University: Little Spokane River at Scotia Road near Newport.

During the synoptic surveys, streamflow data collected by USGS, Spokane County CD, and Whitworth University at their established gaging sites will be adequate for the Little Spokane River mainstem and major tributaries in the project area. Smaller tributaries will require instantaneous streamflow measurements taken at the time of sampling.

Spokane County CD has also deployed continuous recording water temperature units at the following sites:

• Little Spokane River at Elk.

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- West Branch Little Spokane River below Eloika Lake.
- Little Spokane River at Deer Park-Milan Bridge.
- Little Spokane River above Bear Creek.
- Little Spokane River at Chattaroy.
- Little Spokane River at Colbert Road.

Ecology's Eastern Regional Office field staff will deploy additional units at the following locations:

- Deadman Creek.
- Dragoon Creek.
- Little Spokane River above Deadman Creek.
- Little Spokane River below Deadman Creek and above Pine River Park.
- Little Spokane at Griffith Springs.

Air temperature and relative humidity monitoring will be conducted at three sites: near the headwaters of the study area; near Colbert or Pine River Park; and at, or near, the Little Spokane Fish Hatchery.

The data will be used to verify QUAL2K temperature modeling calibration assumptions for these reaches.

Data from previous studies and data collected during this 2010 project will be used to generate nutrient estimates for sub-watershed pollutant load capacities, background and nonpoint load allocations, and point source wasteload allocations. Loading calculations will focus on critical season but cover annual variability as well. Multiple regression analysis or ratio estimator techniques are possible statistical tools.

Sampling Procedures

Collection

Field sampling protocols for synoptic survey data collections will follow Ecology's Environmental Assessment Program (EAP) approved Standard Operating Procedures <u>www.ecy.wa.gov/programs/eap/quality.html</u>:

- EAP013 Determining Global Positioning System coordinates (Janisch, 2006).
- EAP015 Grab sampling Fresh Water (Joy, 2006).
- Invasive Species Moderate Risk Protocols (Ward et al., 2010).

Some protocols described by other agencies have been through peer review and are in common use in the scientific community. In this study the following referenced protocols will be used:

- USGS, 2006. Equal-width increment depth integrated sampling.
- Stevenson and Bahls, 2007. EPA rapid bioassessment periphyton protocols.

All sites will be visited prior to the first synoptic survey to assess any safety concerns or special equipment needs. Permission to enter private property or gain right-of-way access will be clarified before the first survey, and any written documents will be copied and provided to survey crews. Access to Spokane County CD sites on private property will be approved by Spokane County CD before contacting land owners to avoid misunderstandings about access.

All samples collected for the 2010 surveys will be collected from effluents and stream channels in a representative manner. Equal-width increment (EWI) depth-integrated samples (USGS, 2006) will be collected from wider reaches of the mainstem, when feasible, for samples submitted for laboratory analyses. Grab samples may be collected from most narrow, well-mixed tributary sites or narrow, well-mixed mainstem sites. Grab samples will be collected from the thalweg, within free-flowing stream sections, and away from channel boundaries. Grab sampling handling and techniques will follow EAP protocols (Joy, 2006).

Equipment for EWI samples will be examined for adhering material, cleaned, and then rinsed in de-ionized water prior to moving to the next site. At the next site, equipment will be rinsed in local water before a pre-cleaned integration bottle is inserted.

Grab samples will be collected into pre-cleaned containers supplied by Manchester Environmental Laboratory (MEL) as prescribed in MEL's *Lab Users Manual* (MEL, 2008). Sample matrix, container, preservation method, and holding time for each parameter are summarized in Table 7. EWI-type samples will be dispensed into the MEL pre-cleaned containers as well. All samples will be placed in the dark, put on ice, received, and processed by MEL within 48 hours.

Periphyton field sampling protocols are adapted from EPA Rapid Bioassessment Protocols (Stevenson and Bahls, 2007). Periphyton biomass samples will be collected by scraping material from a measured surface area on representative rocks. Three rock 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 speciation. 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., percent filamentous, diatoms, reed canary grass, emergent weeds).

To prevent the spread of invasive species, field crews will visually inspect all equipment surfaces that have contacted water or sediment and remove all mud, algae, plant parts, or any other kind of debris picked up during the sampling operation before leaving each site. If the equipment is free of visible mud or debris, then no more effort will be needed. If the equipment still has visible mud or debris, then staff will clean by scrubbing and rinsing the area until it is visually clean. Felt-soled boots will not be used since reasonable decontamination procedures use ammonia and other chemicals that should be avoided because of potential cross-contamination with samples.

Parameter	Sample Matrix	Container	Preservative	Holding Time
Chlorophyll-a	Surface water and periphyton	1000 mL amber poly	Cool to 4 °C; 24 hrs to filtration	28 days after filtration
Total Organic Carbon	Surface water and point source effluent	125 mL clear poly	1:1 HCl to ph<2; Cool to 4 °C	28 days
Dissolved Organic Carbon	Surface water and point source effluent	125 mL poly with Whatman Puradisc™ 25PP 0.45 µm pore size filters	Filter in field with 0.45 µm pore size filter; 1:1 HCl to ph<2; Cool to 4 °C	28 days
Total Suspended Solids; TNVSS	Surface water and point source effluent	1000 mL poly	Cool to 4 °C	7 days
Alkalinity	Surface water and point source effluent	500 mL poly - no headspace	Cool to 4 °C; Fill bottle completely; Don't agitate sample	14 days
Chloride	Surface water and point source effluent	500 mL poly	Cool to 4 °C	28 days
Total Persulfate Nitrogen	Surface water and point source effluent	125 mL clear poly	H ₂ SO ₄ to pH<2; Cool to 4 °C	28 days
Ammonia	Surface water and point source effluent	125 mL clear poly	H ₂ SO ₄ to pH<2; Cool to 4 °C	28 days
Nitrate/Nitrite	Surface water and point source effluent	125 mL clear poly	H ₂ SO ₄ to pH<2; Cool to 4 °C	28 days
Orthophosphate	Surface water and point source effluent	125 mL amber poly with Whatman Puradisc™ 25PP 0.45 µm pore size filters	Filter in field with 0.45 µm pore size filter; Cool to 4 °C	48 hours
Total Phosphorus	Surface water and point source effluent	60 mL clear poly	1:1 HCl to ph<2; Cool to 4 °C	28 days

Table 7. Containers, preservation methods, and holding times for laboratory samples (MEL, 2008).

TNVSS = Total non-volatile suspended solids.

Documentation

Data and documentation for all surveys will be kept orderly, legible, and secure. Field observations and measurements will be recorded immediately in non-smearing ink or dark pencil on Rite-in-the-Rain[®] paper as they occur. Sheets will be numbered consecutively from the start of the survey run. The following will be recorded:

- The name of the study, station identification number or name, date, time, personnel names, and weather conditions of each site will be clearly noted in a consistent location on the sheets.
- Grab or EWI method of sample collection will be noted.
- For sites with continuous DataSonde recording, instrument identification number, calibration data (or location of data), start and end time of deployment, download file name, time and value of check samples, and specific placement descriptions will be recorded.
- Identification numbers used for lab analysis samples will be recorded. Replicate sample identification numbers will be recorded as well. All information on the sample tag will be recorded in the field notes.
- The identification number of the Hydrolab surveyor, Minisonde, or other equipment used for instantaneous DO, pH, temperature, and conductivity measurements will be noted.
- Staff gage readings or discharge measurement data will be clearly labeled and neatly recorded.

Sample tags will be filled out completely with waterproof pen, dark pencil, or pre-printed ink. Tags or labels will be securely attached to samples. Information will be transferred to the Laboratory Analysis Required form. Tag information will follow MEL requirements that include:

- Study name
- Pre-assigned lab number
- Sample collection location
- Date and time
- Sampler's initial
- Parameter
- Preservatives

Measurement Procedures

Field measurements will follow approved EAP standard operating procedures (SOPs):

- EAP013 Determining Global Positioning System Coordinates (Janisch, 2006).
- EAP023 Winkler Determination of Dissolved Oxygen (Ward, 2007).
- EAP024 Estimating Streamflow (Sullivan, 2007).
- EAP033 Hydrolab[®] DataSonde and MiniSonde Multiprobes (Swanson, 2007).
- EAP044 Continuous Temperature Monitoring of Fresh Water Rivers and Streams Conducted in a Total Maximum Daily Load (TMDL) Project for Stream Temperature (Bilhimer and Stohr, 2009).

Sampling sites will be located on maps, and deviations will be recorded in field notes. Deviations farther than 100 yards will be given a new site number. If the site location does not have easily recognizable landmarks, a Global Positioning System unit reading will be taken to obtain accurate latitude and longitude. Reading will follow EAP SOPs (Janisch, 2006).

Hydrolab[®] multi-probe meters require daily calibration or daily checks (for deployed DataSondes) to meet precision targets. Care will be taken when using multi-probe meters in shallow water that sediment is not disturbed and that probes are completely submerged. Slow velocities also usually require a longer probe equilibration period.

The 48-hour deployments of Hydrolab multi-probe meters during the synoptic surveys will collect DO, pH, temperature, and conductivity data at 10-minute intervals. Data will be downloaded to a secondary portable computer as soon as possible and preferably before the next deployment. Care will be given with deployment of meters to prevent theft or damage while maintaining representative data collection. Meters will be hidden from easy view, secured with cable, and locked to a permanent structure whenever possible. Meters will not be deployed if a rapid increase in streamflow is possible.

Quality assurance samples collected for Winker titration will be collected as close to the meter unit as possible and with the least disturbance and air entrainment. Methods of sample collection may vary by local conditions. Multiple samples are recommended if field staff lack confidence that an undisturbed sample can be collected. Samples will be acid-fixed and titrated at the end of the survey day.

Instantaneous flow measurements will be performed at all sites, not co-located with a gage. Gage flow volumes will be calculated from continuous stage-height records and curves developed prior to, and during, the project. Streamflows will be measured, or staff gage readings taken, at all sites during all field surveys.

If resources are available, field measurements and descriptions of shade, riparian vegetation, and channel geometry characteristics at periphyton sites will be conducted. Temperature TMDL protocols (EAP047 and EAP048) will be used for these measurements (Stohr, in progress).

Quality Objectives

Quality objectives are statements of the precision, bias, and lower reporting limits necessary to address project objectives. Precision and bias together express data accuracy. Quality objectives apply equally to laboratory and field data collected by Ecology, to data used in this study collected by entities external to Ecology, and to modeling and other analysis methods used in this study.

- *Precision* is the degree of agreement between replicate analyses of a sample under identical conditions and is a measure of the random error associated with the analysis, usually expressed as relative percent difference (RPD) or relative standard deviation (RSD) (Lombard and Kirchmer, 2004).
- *Bias* is the systematic or persistent distortion of a measurement process that causes errors in one direction. Some bias can be assessed using blanks, spikes, and check standards
- *Accuracy* is the measure of the difference between an analytical result and the true value, usually expressed as percent. The accuracy of a result is affected by both systematic errors (bias) and random errors (imprecision).

Measurement quality objectives

Measurement quality objectives (MQOs) refer to the performance or acceptance criteria for individual data quality indicators such as precision, bias, and lower reporting limit (Lombard and Kirchmer, 2004). MQOs provide the basis for determining the procedures that should be used for sampling and analysis.

Field studies are designed to generate data adequate to reliably estimate the temporal and spatial variability of that parameter. Sampling, laboratory analysis, and data evaluation steps have several sources of error that should be addressed by MQOs. Accuracy in laboratory measurements can be more easily controlled than field sampling variability. Analytical bias needs to be as low, and precision as high, as possible in the laboratory.

Sampling variability can be controlled somewhat by strictly following standard procedures and collecting quality control samples, but natural spatial and temporal variability can contribute greatly to the overall variability in the parameter value. Resources limit the number of samples that can be taken at one site spatially or over various time intervals. Finally, laboratory and field errors are further amplified by estimate errors in loading calculations and model results.

Precision, bias, and accuracy for water quality data may be measured by one or more of the following quality control procedures: method blanks, matrix spikes, certified reference materials, replicates, positive controls, and negative controls. These are discussed in following sections.

Tables 8 and 9 summarize the MQOs for field and laboratory parameters. The required reporting limits are also included. Continuous or instantaneous Hydrolab meter measurements collected at each sampling event will conform to the quality control parameters in Table 10.

Parameter	Method	Expected Range of Values	Precision (replicate median RSD)	Bias (% deviation from true value)	Reporting Limits and Resolution
Velocity ¹	Marsh McBirney Flowmeter	<0.1 – 10 ft/s	—	n/a	0.01 ft/s
Water Temperature ¹	Hydrolab ^{® 3}	1.0 - 35° C	+/- 0.1° C	n/a	0.01° C
water remperature	Onset TidBit [®]	1.0 - 30° C	+/- 0.2° C	n/a	0.01° C
Relative Humidity	HOBO Pro	0% - 100%	+/- 3.0%	n/a	0.1%
Specific Conductivity ²	Hydrolab [®]	50 – 500 umhos/cm	+/- 0.5%	n/a	0.1 umhos/cm
рН ¹	Hydrolab [®]	6.0 – 9.0 s.u.	0.20 s.u.	n/a	1 to 14 s.u.
Disselved Owners ¹	Hydrolab [®]	1.0 – 12 mg/L	5% RSD	n/a	0.1 - 15 mg/L
	Winkler Titration	1.0 – 12 mg/L	_	n/a	0.1 mg/L

Table 8. Measurement quality objectives for field measurements.

¹ as units of measurement, not percentages. ² as percentage of reading, not RSD. ³ same for both the MiniSonde and DataSonde style of meters.

Table 9. Measurement quality objectives for laboratory analyses.

Parameter	Method	Expected Range of Concentrations	Precision (replicate median RSD)	Reporting Limits and Resolution
Chloride	EPA 300.0	0.3 – 100 mg/L	20% RSD ¹	0.1 mg/L
Total Suspended Solids; TNVSS	SM 2540D	1 – 10,000 mg/L	20% RSD ¹	1 mg/L
Alkalinity	SM 2320B	20 – 200 mg/L as CaCO₃	20% RSD ¹	5 mg/L
Ammonia	SM 4500-NH ₃ H	<0.01 – 30 mg/L	20% RSD ¹	0.01 mg/L
Dissolved Organic Carbon	EPA 415.1	<1 – 20 mg/L	20% RSD ¹	1 mg/L
Nitrate/Nitrite	4500-NO ₃ I	<0.01 – 30 mg/L	20% RSD ¹	0.01 mg/L
Total Persulfate Nitrogen	SM 4500-NB	0.5 – 50 mg/L	20% RSD ¹	0.025 mg/L
Orthophosphate	SM 4500-P G	0.01 – 5.0 mg/L	20% RSD ¹	0.003 mg/L
Total Phosphorous	SM 4500-P F	0.01 – 10 mg/L	20% RSD ¹	0.005 mg/L
Total Organic Carbon	EPA 415.1	<1 – 20 mg/L	20% RSD ¹	1 mg/L
Biochemical Oxygen Demand	EPA 405.1	<1 – 14 mg/L	20% RSD ¹	2 mg/L
Chlorophyll-a	SM 10300	$1 - 1000 \text{ mg/m}^2$	20% RSD ¹	0.1 µg/L
Ash-free Dry Weight	SM 10300	1 – 1000 mg/m ²	20% RSD ¹	1 mg/L

Precision replicate error values include laboratory and field variability.

¹ Replicate results with a mean of less than or equal to 5 times the reporting limit will be evaluated separately. TNVSS = Total non-volatile suspended solids.

SM = Standard Methods for the Examination of Water and Wastewater, 20th Edition (APHA, AWWA and WEF, 1998). EPA = EPA Method Code.

Table 10 Hydrolab [®] equipment individual probe quality control requirement						
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	1 able 10. H	vdrolab [*] edulbi	nent individual	brobe duality	v control rec	iuirements.

Parameter	Replicate Samples	Field Calibration Check Standards	Calibration Drift End Check
Dissolved Oxygen	RPD ≤ 20%	n/a	±4%
рН	± 0.2 pH units	± 0.2 pH units	± 0.2 pH units
Temperature	± 0.3 °C	n/a	n/a
Conductivity	RPD ≤ 10%	± 10 %	± 10 %

Quality objectives for modeling or other analysis

Statistical evaluations and models used in the data analysis will be assessed. Model resolution and performance will be measured using the root-mean-square-error (RMSE) or Nash-Sutcliffe coefficient. The RMSE is a commonly used measure of model variability (Reckhow et al., 1986). The RMSE is defined as the square root of the mean of the squared difference between the observed and simulated values.

Since DO and pH are biologically mediated, no set RMSE will be established now. Nash-Sutcliffe coefficient of efficiency (Nash and Sutcliffe, 1970) measures model errors in estimating the mean or variance of the observed data sets. It is more sensitive to outliers in continuous simulation output than the RMSE. A Nash-Sutcliffe coefficient between 0 and 1 is desirable. Sensitivity analysis will be conducted on the calibrated QUAL2Kw model results by varying key parameters and boundary conditions by 10%.

Quality Control Procedures

Field and laboratory

Quality control measurements for grab samples will be taken at intervals summarized in Table 11. Meter DO measurements may be compared to Winkler samples or a second meter that has been allowed to equilibrate to local conditions. The meter pH, temperature, and conductivity measurements may be compared to standard solutions, a hand-held thermometer reading, or a second meter. Pre- and post-deployment calibration checks will be conducted and recorded with survey data.

Parameter	Field Blanks	Field Replicates	Lab Check Standard	Lab Method Blanks	Lab Replicates	Matrix Spikes
Field						
Velocity	n/a	1/run	n/a	n/a	n/a	n/a
рН	n/a	2/run	n/a	n/a	n/a	n/a
Temperature	n/a	2/run	n/a	n/a	n/a	n/a
Dissolved Oxygen	n/a	1/5 samples	n/a	n/a	n/a	n/a
Specific Conductivity	n/a	2/run	n/a	n/a	n/a	n/a
Laboratory						
Chlorophyll-a	n/a	1/run*	n/a	n/a	1/20 samples	n/a
Total Organic Carbon	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Dissolved Organic Carbon	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Total Suspended Solids	1/survey	1/run	1/run	1/run	1/20 samples	n/a
Alkalinity	1/survey	1/run	1/run	1/run	1/20 samples	n/a
Chloride	1/survey	1/run	1/run	1/run	1/20 samples	1/10 samples
Total Persulfate Nitrogen	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Ammonia Nitrogen	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Nitrate & Nitrite Nitrogen	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Orthophosphate P	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples
Total Phosphorus	1/survey	1/run	1/run	1/run	1/20 samples	1/20 samples

*At least one field replicate will be collected during a daily sample run. Two additional samples will be collected at random over the course of the survey.

A second multi-probe meter or DO Winkler sample will be used to verify calibration of Hydrolab multi-probes as directed under the SOP EAP033. Deployed DataSondes for 48-hour diel continuous monitoring require independent quality control measurements at the time of deployment, at least twice during the monitoring period, and upon removal. Measurements should include a Winkler DO sample, and Hydrolab multi-probe readings of pH, DO, temperature, and conductivity. An effort will be made to catch periods of maximum or minimum ranges.

Total variability for laboratory analysis will be assessed by collecting replicate samples. Sample precision will be assessed by collecting replicates for 10-20% of samples in each survey (Table 11). Field blanks and filter blanks will be submitted with each sampling run to assess some areas of bias. MEL routinely duplicates sample analyses in the laboratory (Lab Duplicate) to determine laboratory precision. The difference between field variability and laboratory variability is an estimate of the sample field variability.

MEL will inform the project manager or principle investigator as soon as possible if any sample is lost, damaged, has a lost tag, or gives an unusual result.

Data Management Procedures

Field measurement data will be entered from the field book into EXCEL® spreadsheets (Microsoft, 2007) as soon as practical after returning from the field. Hydrolab recovered data and gage recording data likewise will be downloaded into a central database. This database will be used for preliminary analysis and to create a table to upload data into Ecology's EIM System. The database will be held in a computer space with a daily automatic back-up routine to a remote/separate computer.

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.

All continuous data will be stored in a project database that includes station location information and data quality assurance information. This database will facilitate summarization and graphical analysis of the DO and pH data and also create a data table to upload the data to Ecology's statewide EIM geospatial database.

An EIM user study ID (jjoy0007) with data collected from the 2004-06 surveys has been created for this TMDL study. All monitoring data from this set of surveys will be available under the same user study ID via the internet once the project data has been validated. The URL address for this geospatial database is: <u>apps.ecy.wa.gov/eimreporting</u>. All 2010 data will be uploaded to EIM by the EIM engineer after all data have been reviewed for quality assurance and finalized.

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

Audits and Reports

MEL will supply quality assurance statements with paper copies of the laboratory data as it is entered into LIMS.

The project manager will submit the draft and final technical study report to Ecology's Eastern Regional Office, Water Quality Program, TMDL lead for this project, according to the project schedule.

Data Verification and Validation

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

Field staff will check field notebooks for missing or improbable measurements before leaving each site. The EXCEL® Workbook file containing field data will be labeled DRAFT until data verification is complete. Data entry will be checked against the field notebook data for errors and omissions. Missing or unusual data will be brought to the attention of the project manager for consultation. Valid data will be moved to a separate file labeled FINAL.

The field lead will check data received from LIMS for omissions against the Request for Analysis forms. Data can be in EXCEL® spreadsheets (Microsoft, 2007) or downloaded tables from EIM. These tables and spreadsheets will be located in a file labeled DRAFT until data verification is completed. Field replicate sample results will be compared to quality objectives in Tables 8 through 10. The project manager will review data requiring additional qualifiers.

After data verification 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 EAP 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. Semi-annual reports will be available during the data collection period of the project.

Data Quality (Usability Assessment)

Study data usability

The field lead will verify which measurement and data quality objectives have been met for each monitoring station. For example, if the objectives have not been met, such as if the %RSD for phosphorus replicates exceeds the MQO or a Hydrolab shows signs of malfunctioning, then the field lead and project manager will decide whether to delete non-credible data or how to qualify the data. All data considered credible, including non-detected analytes, will be available in EIM and for use in the analyses with appropriate qualifiers and comments taken into account. Data may be eliminated from statistical or graphical analysis after careful consideration of all quality control processes.

The field investigator or project manager will produce a data summary and quality assurance report that will include at a minimum: site descriptions, data quality assurance notes, calculations of quality assurance measures and comparison to quality assurance project plan MQOs, and graphs of all continuous data.

Once quality steps have been completed, data are fit for analysis. Data analysis will include evaluation of data distribution characteristics and, if necessary, appropriate distribution of transformed data. Censored data will be included in data analyses using appropriate statistical techniques. Estimation of univariate statistical parameters and graphical presentation of the data (box plots, time series, and regressions) will be made using WQHYDRO (Aroner, 2007), EXCEL[®] (Microsoft, 2007), or SYSTAT [®] (SYSTAT, 2009) software.

Usability of results from modeling or other analysis

Evaluation of the causes of DO and pH criteria violations in the Little Spokane River watershed will require using historical data with the data collected in this 2010 survey. Good comparability is expected between these data and most data previous collected in the Little Spokane River watershed. Work performed by WSU/WWRC (Barber et al., 2007) was conducted under an Ecology approved quality assurance plan with control measures similar to this one (Cichosz et al., 2005). Ecology ambient monitoring program data are also collected under a quality assurance plan (Ecology, 2010a). Work performed by Pend Oreille CD and Spokane County CD had quality assurance plans approved by Ecology (POCD, 1999; SCCD, 2003). Stream gage data measured by Spokane County CD and USGS is performed under tight quality control guidelines.

Some changes in land use in the Lower Spokane River watershed have occurred since the late 1990s, especially a reduction in the number of dairies in tributary watersheds. Nonparametric paired tests will be used to determine if nutrient loads at individual sites have significantly changed between earlier and recent surveys. If no statistical difference is observed, then newer and older data will be used together to calculate annual and seasonal loads.

All modeling and statistical method assumptions will be transparent. Graphical representation of statistical and model results will be available and used in report or presentation discussions. Observed and model simulations will be shown together for visual comparison. Variables, coefficients, and boundary conditions will be tabularized for the calibrated model and scenarios.

The assumptions behind the statistical calculations and calibrated model, and the uncertainty in the results for current conditions, will be fully reviewed before future or natural condition scenarios are evaluated. A margin of safety will be considered to apply to scenarios through discussion with regional Ecology TMDL staff, EAP modeling staff, and members of the Little Spokane River Watershed Advisory Committee. The margin of safety will include uncertainty with changes in past and future land use, streamflows, riparian condition, and effectiveness of nonpoint load reduction activities.

Project Organization

Table 12 summarizes the primary individuals involved in the study and their contact information. Outside agencies will be coordinated through single individuals to avoid miscommunications.

Table 12.	Organization of	project staff and	responsibilities.

Staff	Title	Responsibilities
Karin Baldwin Water Quality Program Eastern Regional Office (509) 329-3472	Overall Project Lead	Acts as point of contact between EAP staff and interested parties. Coordinates information exchange. Forms technical advisory team and organizes meetings. Reviews the QAPP and technical report. Prepares and implements TMDL report for submittal to EPA.
David T. Knight Water Quality Program Eastern Regional Office (509) 329-3590	Unit Supervisor of Project Lead	Approves TMDL report for submittal to EPA.
Joe Joy Eastern Operations Section EAP (360) 407-6486	Project Manager	Writes the QAPP. Coordinates field surveys with principal investigator. Assists with writing the data summary report.
Scott Tarbutton Eastern Operations Section EAP (509) 329-3476	Principal Investigator	Oversees field operations, recruits field assistants, and coordinates with the laboratory. Collects field samples and records field information. Tentatively writes data summary under the supervision of the project manager.
Gary Arnold Eastern Operations Section EAP (509) 454-4244	Section Manager of Project Manager	Approves the QAPP and the data summary report. Schedules and assigns resources to complete the technical TMDL report.
Stuart Magoon Manchester Environmental Laboratory, EAP (360) 871-8801	Director	Provides laboratory staff and resources, sample processing, analytical results, laboratory contract services, and quality assurance/quality control (QA/QC) data. Approves the QAPP.
William R. Kammin EAP (360) 407-6964	Ecology Quality Assurance Officer	Provides technical assistance on QA/QC issues. Reviews the draft QAPP and approves the final QAPP.
Rick Noll Spokane County Conservation District (CD) (509) 535-7274	Conservation District Contact	Provides Spokane County CD gage data, directs site access requests through proper channels, reviews drafts and final QAPP and reports. Prepares and implements TMDL report with the Eastern Regional Office project lead.
Deb Geiger (tentative) Spokane County (509) 238-6607	Spokane County Contact	Provides permission to sample the Colbert Landfill outfall and provides ancillary data.
Guy Campbell Washington Dept. of Fish and Wildlife (509) 625-5169	Little Spokane River Fish Hatchery Manager	Provides permission to sample the Little Spokane River Hatchery outfall at Griffith Springs and provides ancillary data.

EAP - Environmental Assessment Program.

EIM – Environmental Information Management system.

QAPP - Quality Assurance Project Plan.

Project Schedule

After the 2010 synoptic surveys sample collection is completed, the project schedule may depend on other resources and other scheduled work in the Spokane River basin. A summary of the field and laboratory data from the 2010 synoptic surveys is planned to formally organize the information in preparation for the *Water Quality Improvement Report* (WQIR) analyses and writing (Table 13).

The WQIR schedule should not be entered into Ecology's Activity Tracker database until the work is assigned and scheduled. Work on the Little Spokane River DO & pH TMDL WQIR could be delayed for an extended time. The lead staff of the Little Spokane River TMDLs also has responsibility for the Hangman Creek DO and pH TMDL WQIR. Work on that TMDL could take an inordinate amount of time since new water quality policies are being conceived and tested there.

Field and laboratory work	Due date	Lead staff
Field work completed	September 2010	Joe Joy/Jim Ross & EOS staff
Laboratory analyses completed	October 2010	
Environmental Information System (EIM) of	latabase	
EIM user study ID	jjoy0007	
Product	Due date	Lead staff
EIM data loaded	November 2010	Dan Sherratt
EIM quality assurance	December 2010	Andy Albrecht
EIM complete	January 2011	Dan Sherratt
Data Summary Report		
Activity Tracker code	11-014	
Author lead	Scott Tarbutton	
Schedule	Due date	
Draft due to supervisor	March 2011	
Draft due to client/peer reviewer	April 2011	
Draft due to external reviewer(s)	April 2011	
Final (all reviews done) due to EAP publications coordinator	May 2011	
Final report due on web	June 2011	

Table 13. Proposed schedule for completing field and laboratory work, data entry into EIM, and data summary report.

EOS – Ecology's Eastern Regional office.

Laboratory Budget

Laboratory costs associated with the two 2010 synoptic surveys are estimated at \$35,240 and are detailed in Table 14.

		No. of sites	QA samples survey	Price (\$)	Total per Survey (\$)	No. of surveys	Analysis cost/task (\$)
Synoptic Su	urveys						
Total Phospl	horus	52	5	19	1,065	2	2,131
Orthophosph	nate - P	52	5	16	887	2	1,775
Nitrate + Niti	rite N	52	5	14	770	2	1,539
Total Persulf	fate N	52	5	16	887	2	1,775
Ammonia - N	NH3	52	5	14	770	2	1,539
Chloride		52	5	14	770	2	1,539
BOD5		8	1	57	514	2	1,028
Total Organi	c Carbon	52	5	34	1,953	2	3,906
Dissolved O	rganic Carbon	52	5	37	2,128	2	4,257
TSS + TNVS	SS	26	5	25	773	3	2,318
Alkalinity		52	5	18	1,006	2	2,012
Perinhuton	Ash-free dry weight	12	1	11	148	2	297
renpriyton	Chlorophyll-a	12	1	57	742	2	1,485
				Totals	\$ 12,413		\$ 25,599
Tributary S	urveys						
Total Phospl	horus	16	2	19	336	2	673
Orthophosph	nate - P	16	2	16	280	2	561
Nitrate + Niti	rite N	16	2	14	243	2	486
Total Persulf	fate N	16	2	16	280	2	561
Ammonia - NH3		16	2	14	243	2	486
Chloride		16	2	14	243	2	486
BOD5		3	1	57	228	2	457
Total Organic Carbon		16	2	34	617	2	1,233
Dissolved Organic Carbon		16	2	37	672	2	1,344
TSS + TNVSS		16	2	25	449	3	1,346
Alkalinity		16	2	18	318	2	635
Periphyton	Ash-free dry weight	9	1	11	114	2	228
	Chlorophyll-a	9	1	57	571	2	1,142
Totals \$ 4,595 \$ 9,638							

Table 14. Laboratory analyses cost estimate. ¹

 $^{\rm 1}$ Costs include 50% discount for MEL prices for Fiscal Year 2011.

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Appendices

Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Ambient: Background or away from point sources of contamination.

Analyte: Something that is analyzed.

Anthropogenic: Human-caused.

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

Bioassessment: A system of collecting samples and taking measurements to determine the health and diversity of a biological community or its potential.

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.

Critical condition: When the physical, chemical, and biological characteristics of the receiving water environment interact with the effluent to produce the greatest potential adverse impact on aquatic biota and existing or designated water uses. For steady-state discharges to riverine systems, the critical condition may be assumed to be equal to the 7Q10 flow event unless determined otherwise by the department.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each waterbody or segment, regardless of whether or not the uses are currently attained.

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

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

Diurnal: Daily; related to actions which are completed in the course of a calendar day, and which typically recur every calendar day (e.g., diurnal temperature rises during the day, and falls during the night).

Ecoregion: A geographic region defined by similar geological, biological, and climate conditions.

Eutrophic: Nutrient rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Hyporheic: The area beneath and adjacent to a stream where surface water and groundwater intermix.

Leachate: Liquid that has come in contacted with a solid material and that has picked-up chemicals and other contaminates.

Load allocation: The portion of a receiving waters' loading capacity attributed to one or more of its existing or future sources of nonpoint pollution or to natural background sources.

Loading capacity: The greatest amount of a substance that a waterbody can receive and still meet water quality standards.

Macrophytes: Submerged, emergent, or floating aquatic plants visible to the naked eye.

Mainstem: The primary channel of a river system contributed to by tributaries.

Municipal separate storm sewer systems (MS4): A conveyance or system of conveyances (including roads with drainage systems, municipal streets, catch basins, curbs, gutters, ditches, manmade channels, or storm drains): (1) owned or operated by a state, city, town, borough, county, parish, district, association, or other public body having jurisdiction over disposal of wastes, stormwater, or other wastes and (2) designed or used for collecting or conveying stormwater; (3) which is not a combined sewer; and (4) which is not part of a Publicly Owned Treatment Works (POTW) as defined in the Code of Federal Regulations at 40 CFR 122.2.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

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: A physical chemical or biological property whose values determine environmental characteristics or behavior.

Periphyton: Algae and other organisms growing on the bottom or on other submerged surfaces of a stream, river, or lake.

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 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.

Reach: A specific portion or segment of a stream.

Reaeration: Adding air to water through physical, mechanical, chemical, or biological means.

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

Salmonid: Any fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. <u>www.fws.gov/le/ImpExp/FactSheetSalmonids.htm</u>.

Streamflow: Discharge of water in a surface stream (river or creek).

Surrogate measures: To provide more meaningful and measurable pollutant loading targets, EPA regulations [40 CFR 130.2(i)] allow other appropriate measures, or surrogate measures in a TMDL. The Report of the Federal Advisory Committee on the Total Maximum Daily Load (TMDL) Program (EPA, 1998) includes the following guidance on the use of surrogate measures for TMDL development:

When the impairment is tied to a pollutant for which a numeric criterion is not possible, or where the impairment is identified but cannot be attributed to a single traditional "pollutant," the state should try to identify another (surrogate) environmental indicator that can be used to develop a quantified TMDL, using numeric analytical techniques where they are available, and best professional judgment (BPJ) where they are not.

Synoptic survey: Data collected simultaneously or over a short period of time.

Thalweg: The deepest and fastest moving portion of a stream.

Total maximum daily load (TMDL): 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.

Total suspended solids (TSS): Portion of particulate solids in a water sample retained by a filter after drying at 103 - 105°C.

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.

Acronyms and Abbreviations

Biochemical oxygen demand
Carbonaceous biochemical oxygen demand
Conservation District
(See Glossary above)
Dissolved organic carbon
For example
Environmental Assessment Program (Department of Ecology)
Washington State Department of Ecology
Environmental Information Management database
U.S. Environmental Protection Agency
Equal width increment
And others
In other words
Laboratory information management system
Little Spokane River
Manchester Environmental Laboratory
Measurement quality objective
Quality assurance
River mile
Relative percent difference
Relative standard deviation
Standard operating procedures
Soluble reactive phosphorus
Spokane Valley-Rathdrum Prairie (aquifer)
(See Glossary above)
Total non-volatile suspended solids

TOC	Total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish & Wildlife
WDOT	Washington State Department of Transportation
WQIP	Water Quality Implementation Plan
WRIA	Water Resources Inventory Area
WWRC	Washington Water Research Center
WSU	Washington State University
WWTP	Wastewater treatment plant

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)
mL	milliliters
s.u.	standard units
ug/Kg	micrograms per kilogram (parts per billion)
µg/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter
μS/cm	microsiemens per centimeter, a unit of conductivity

Appendix B. QUAL2Kw Framework Description

Water quality computer modeling will be conducted using QUAL2Kw (Pelletier and Chapra, 2003). QUAL2Kw will be used for critical DO and pH condition modeling tasks. The model uses kinetic formulations for simulating DO and pH in the water column similar to those shown in Figure 10 and Table 15. QUAL2Kw will be used to analyze the fate and transport of water quality variables relating to nutrients, periphyton, DO, and pH interactions in the water column. The water quality model will be developed to simulate dynamic variations in water quality of the Little Spokane River. The water quality model will be calibrated and corroborated using data collected during the two synoptic surveys and any historical data collected to the extent possible.

QUAL2K will be applied by assuming that streamflow remains constant (i.e., steady flows) for a given condition such as a 7-day or 1-day period (using daily average flows), but key variables other than flow will be allowed to vary with time over the course of a day. For QUAL2K temperature simulation, the solar radiation, air temperature, relative humidity, headwater temperature, and tributary water temperatures are specified or simulated as diurnally varying functions.



Figure 10. Model kinetics and mass transfer processes in QUAL2Kw.

The state variables are defined in Table 15. Kinetic processes are dissolution (ds), hydrolysis (h), oxidation (x), nitrification (n), denitrification (dn), photosynthesis (p), death (d), and respiration/excretion (r).

Mass transfer processes are reaeration (re), settling (s), sediment oxygen demand (SOD), sediment exchange (se), and sediment inorganic carbon flux (cf). The subscript x for the stoichiometric conversions stands for chlorophyll-a (a) and dry weight (d) for phytoplankton and bottom algae, respectively. For examples:

- r_{px} and r_{nx} are the ratio of phosphorus and nitrogen to chlorophyll-a for phytoplankton, or the ratio of phosphorus and nitrogen to dry weight for bottom algae.
- rdx is the ratio of dry weight to chlorophyll-a for phytoplankton or unity for bottom algae.
- r_{nd} , r_{pd} , and r_{cd} are the ratios of nitrogen, phosphorus, and carbon to dry weight.

Variable	Symbol	Units*	Measured as
Conductivity	S	μmhos	COND
Inorganic suspended solids	m_i	mgD/L	TSS-VSS
Dissolved oxygen	0	mgO ₂ /L	DO
Slow-reacting CBOD	C_s		-
Fast-reacting CBOD	$C_{f,}$		r_{oc} * DOC or CBODU
Organic nitrogen	n _o	μgN/L	TN – NO3N NO2N– NH4N
Ammonia nitrogen	n_a		NH4N
Nitrate nitrogen	n _n		NO3N+NO2N
Organic phosphorus	p_o	μgP/L	TP - SRP
Inorganic phosphorus	p_i		SRP
Phytoplankton	a_p	µgA/L	CHLA
Detritus	m_o	mgD/L	r_{dc} (TOC – DOC)
Alkalinity	Alk	mgCaCO ₃ /L	ALK
Total inorganic carbon	C_T	mole/L	Calculation from pH and alkalinity
Bottom algae biomass	a_b	gD/m ²	Periphyton biomass dry weight
Bottom algae nitrogen	IN_b	mgN/m ²	Periphyton biomass N
Bottom algae phosphorus	IP_b	mgP/m^2	Periphyton biomass P

Table 15. QUAL2K model state variables (Chapra and Pelletier, 2003).

* mg/L = g/m³

D = dry weight.

A = chlorophyll-a.

 r_{oc} = stoichiometric ratio of oxygen for hypothetical complete carbon oxidation (2.69).

The following are measurements that are needed for comparison with model output:

- COND = specific conductance (μ mhos/cm).
- TSS = total suspended solids (mgD/L).
- VSS = volatile suspended solids (mgD/L).
- DO = dissolved oxygen (mgO_2/L) .
- DOC = dissolved organic carbon (mgC/L).
- NO3N = nitrate nitrogen (μ gN/L).
- NO2N = nitrite nitrogen (μ gN/L).
- NH4N = ammonium nitrogen (μ gN/L).
- TP = total phosphorus ($\mu gP/L$).

- SRP = soluble reactive phosphorus ($\mu gP/L$).
- CHLA = chlorophyll-a (µgA/L).
- TOC = total organic carbon (mgC/L).
- ALK = alkalinity (mgCaCO₃/L).
- pH = pH.
- TEMP = temperature ($^{\circ}$ C).
- TKN = total kjeldahl nitrogen (μ gN/L) or TN = total nitrogen (μ gN/L).