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Quality Assurance Project Plan: Little Spokane River Watershed Total Maximum Daily Load Study

by

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Approvals:

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Jon Jones, Eastern Regional Office	11-1-05 Date

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1 PROJECT ORGANIZATION AND SCHEDULE

This project is a collaborative effort between Washington Department of Ecology, Washington State University and stakeholders. The roles and responsibilities of staff involved in this project are provided below:

- Michael Barber, Project Co-Manager, Washington State Water Research Center, Washington State University. In charge of technical issues, WSU task assignments, and report preparations (509-335-5531).

- Shulin Chen, Project Co-Manager, Washington State Water Research Center, Washington State University. Responsible for the contract and budgetary issues as well as quality assurance (509-335-3743).

- Gubin Fu, PhD Graduate Student Assistant, Department of Biological Systems Department, Washington State University. Responsible for data collection, analysis, processing, illustration, and report preparation (509-335-1100).

- Thomas Cichosz, Research Associate, Washington State Water Research Center, Washington State University. Responsible for field data coordination and collection and data input (509-335- 4497).

- Jonathan Lomber, Research Technologist, Department of Biological Systems Engineering, Washington State University. Responsible for laboratory operations, analyses, and data handling (509-335-1292).

- Joe Joy, Washington Department of Ecology, Headquarters, Responsible for technical oversight (360-407-6486).

- Karol Erickson, Unit lead of the Watershed Studies Unit of the Environmental Assessment Program. Washington State Department of Ecology. Headquarters. Contract Officer (360-407-6694).

- Paul Turner, Washington State Department of Ecology, Eastern Regional Office. Overall TMDL lead (509-329-3580).

- David Knight, Unit Supervisor, Water Quality Program, Washington State Department of Ecology, Eastern Regional Office. Responsible for overall project oversight (509-329-3590).

- Elaine Snouwaert, Washington State Department of Ecology, Eastern Regional Office. Responsible for outreach efforts (509-329-3503).

During the study, the project team obtained assistances from many agencies and individuals, especially the Spokane County Conservation District and the Little Spokane Watershed Management Group.

The proposed schedule for the TMDL project is as follows:

Initial Phase I schedule:

- Start Date: January 1, 2004
- Internal "kick-off" meeting: December 12, 2003
- Meeting with Advisory Committee: February 3, 2004
- Draft QAPP for Ecology's review: March 15, 2004
- Draft QAPP for external stakeholder review: April 30, 2004
- Public meeting: Early May, 2004
- Draft QAPP July 19, 2004
- Final QAPP: June 30, 2005

Tentative Phase II schedule:

- TMDL survey sampling: December, 2004 – May, 2006*
- Data review and analysis: June – August, 2006
- Draft final report: November, 2006
- Final report: December, 2006

* Fifteen months of sampling will occur. The final 3 months may be non-continuous with the first 12 months as described in Section 6.4 of this document.

2 INTRODUCTION

2.1 Problem Statement

As illustrated in Figure 1, the Little Spokane River (LSR) drainage basin consists of a 700 square mile drainage area that includes regions located in north-central Spokane County, southern Pend Oreille County, and southeastern Stevens County in northeast Washington, as well as Bonner County in the state of Idaho. The watershed has been designated as Water Resource Inventory Area (WRIA) number 55. The majority of the watershed, approximately 417 square miles, is in Spokane County. Stevens and Pend Oreille Counties make up approximately 260 square miles of the watershed. Only 23 square miles is in Bonner County, Idaho. The river is one of the two major tributaries to the Spokane River (Latah/Hangman Creek being the other). The river discharges into the Spokane River at River Mile (RM) 56.3 downstream of Nine Mile Dam and upstream of Long Lake.

Several streams and rivers in the LSR drainage basin are on the 1998 and proposed 2002/2004 303(d) list because of violations of one or more water quality criteria. The Little Spokane Water Quality Assessment (POCD, 2000) was conducted in 2000 in accordance to the Quality Assurance and Water Quality Monitoring Program Plan developed by the Pend Oreille Conservation District (POCD). This plan was reviewed and approved by the Washington State Department of Ecology (Ecology) Watershed Assessment Section. The Ecology Water Quality Program further selected the basin for a total maximum daily load (TMDL) assessment. The State of Washington Water Research Center (SWWRC), in cooperation with the Ecology Environmental Assessment Program (EAP), has been asked to design and conduct the TMDL study for the basin. This document summarizes the findings from historical data and from discussions with local agencies pertaining to water quality problems in the basin. Based upon these findings, a TMDL study project design and quality assurance project plan is described.

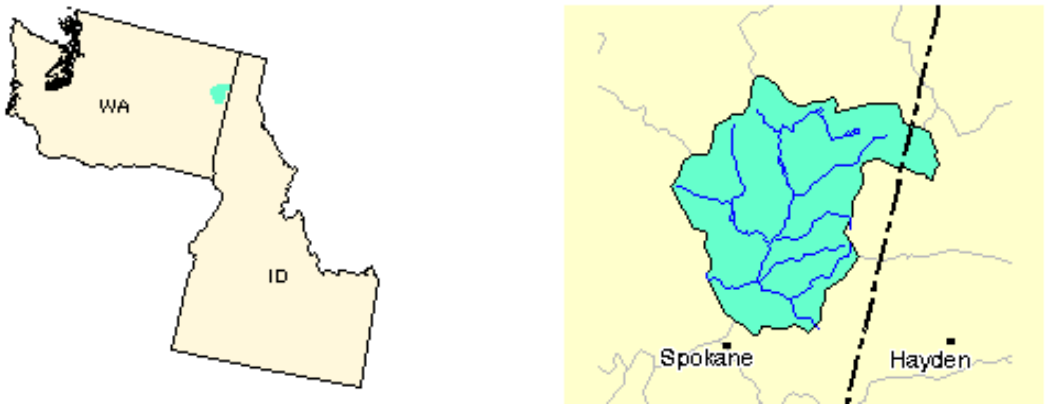


Figure 1. Vicinity map of the Little Spokane River region

2.2 Objectives of Study

This report contains a historic data and data gap analysis that are consistent with Ecology's water quality assurance project plans (QAPP) as well as a proposed monitoring and analysis program for a TMDL study on the Little Spokane River. Consequently, the report has multiple objectives. The QAPP portion has been prepared to meet the following objectives:

- Compile all available water quality bioassessment, land use and streamflow data for the Little Spokane River
- Identify areas of known water quality impairments and with a lack of data
- Identify factors that could limit the use of data for TMDL analysis
- Conduct historical data assessment to recognize the trend of water quality improving or deteriorating in impaired areas
- Analyze the interrelationship of the chemical parameters of water such as dissolved oxygen, pH, temperature and fecal coliform
- Identify potential point and nonpoint sources
- Identify data gaps needed for developing TMDL

The objectives of the TMDL study are to:

- Collect water quality data from streams in the Little Spokane River watershed to characterize the basin's water quality in terms of temperature, dissolved oxygen, pH, turbidity, fecal coliform bacteria, and nutrients (nitrogen and phosphorus)
- Compare resulting concentration data to existing water quality standards to determine what areas are not meeting standards, if any
- For those areas not meeting standards, develop Total Maximum Daily Loads for the appropriate parameters. Develop wasteload allocations for point sources and load allocations for nonpoint sources
- Collect screening level data for pesticides and herbicides.

2.3 Basin Information

2.3.1 Population

Within Spokane County, the Little Spokane Watershed (WRIA 55) encompasses the City of Deer Park, the Spokane North Metro Interim Urban Growth Area (IUGA), and unincorporated portions of Spokane County. These regions represent rapidly growing areas within the County. For example, previous population estimates for these areas, including the North Rural area, range from approximately 35,000 (calculated from Spokane County Long-Range Planning Regional Transportation Traffic Analysis Zone provided by the Spokane County Conservation District (SCCD)) to approximately 45,000 (estimated from 1990 census tracts). By comparison, the 2000 Census data indicated that the population of WRIA 55 in Spokane County increased to 95,201 (Golder, 2003). Of this, approximately 56,500 people live in the unincorporated Spokane County

portion of the watershed. The remainder live in the incorporated City of Spokane IUGA region or in the other two counties.

Pend Oreille County's Planning Department estimates their portion of population within the Little Spokane River watershed as approximately 2,750. The population growth trend is expected to continue in this area as substantiated by the number of subdivision applications, building permits and vacant tracts of land for sale, with the most desirable tracts of land being adjacent to the Little Spokane River and its tributaries. In Stevens County, residences are generally located near Highway 395. The population in the southeastern Stevens County is estimated to be less than or equal to the 2,750 of Pend Oreille County.

The population density of the Little Spokane River watershed, produced by the Washington State Department of Ecology, is shown in Figure 2. The spatial distribution shows that Deer Park and Spokane North Metro IUGA have the highest population density (darker colors).

2.3.2 Topography and Drainage

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

Because of similar basin characteristics and convenience in assimilating information, the watershed has been subdivided into the seven major subbasins shown in Figure 4. These subbasins are:

(1) Upper Little Spokane River, covering the mainstem of the Little Spokane River above Chattaroy;
(2) West Branch of the Little Spokane River;
(3) Dragoon Creek;
(4) Deadman Creek, including the Peone Creek and the Deadman Creek drainage areas;
(5) Deer Creek;
(6) Deep Creek; and
(7) Lower Little Spokane River below Chattaroy.

Dragoon Creek subbasin lies mostly between 2,000 feet and 2,200 feet above mean sea level. Several mesas (such as Orchard Bluff, Green Bluff, Foothills, Pleasant Prairie, and Orchard Prairie) and the valley between the mesas form a large portion of the area east of the Little Spokane River. The mesas rise about 400 feet above their bases, and the tops of the mesas are generally between 2,300 and 2,400 feet above sea level (Chung 1975).

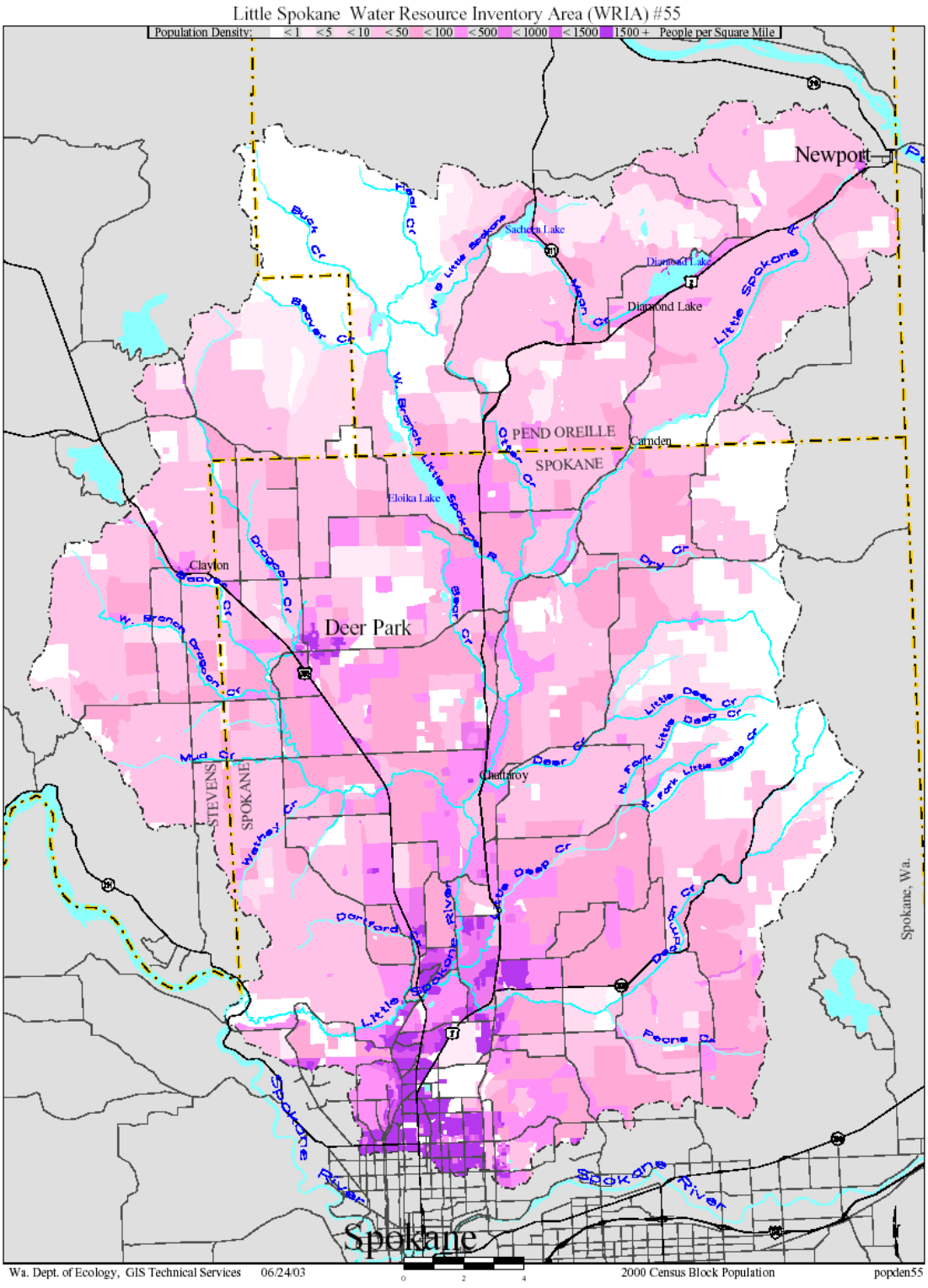


Figure 2. Population Densities in Little Spokane Watershed

The impact of these mesas and the topography in general will likely be seen in models predicting runoff at the watershed scale. The 10-meter Digital Elevation Map (DEM) in Figure 5 shows the topographical spatial distribution within the watershed and several prominent features can be observed.

2.3.3 Geologic Setting

Plutonic and metamorphic rocks of pretertiary age (more than 63 million years) underlie the entire area. These basement rocks form the mountains that surround the drainage basin. During late Tertiary time (1 million to 63 million years ago) extensive basaltic lava flows flooded a vast region and blocked stream drainages, including the ancestral Spokane River. The blockages formed lakes into which sediments eroded from the higher lands were deposited. The resulting lake beds underlie and are interbedded with the basalt, particularly southwest of Spokane.

With cessation of the outpouring of the basalt, the Spokane River carved a deep trench through the basalt and lakebeds. This trench, later buried beneath Quaternary glacial deposits (less than 1 million years ago), probably now underlies the Hillyard area and turns westward along the Little Spokane River and northwestward down the present valley of the Spokane River.

During Pleistocene time (less than 1 million but more than 10,000 years ago), extensive glaciers moved into the area from north and east, stopping just south of Milan, and a short distance east of Spokane in the Spokane River Valley (Cline 1969; Chung 1975).

Erosion by the ice and the intermittent torrential glacial streams left a number of basalt-capped mesas. At various times since, the edges of the mesas have given away in landslides. The glaciers also brought much debris that was deposited in a variety of ways, some directly by ice (morainal deposits), some in glacial lakes (glaciolacustrine deposits), some by streams of glacial melt water (glaciofluvial deposits), and some, like the Palouse Formation, by long-distance wind transport (Cline 1969; Chung 1975).

During the Holocene (recent) time, following the retreat and disappearance of the glaciers, the rivers, principally the Little Spokane River, have been depositing alluvium along their channels, and winds have blown loose sand to form dunes at several places in the basin.

The valley of the lower Little Spokane River, an area from a line about two miles north of Chattaroy to the Little Spokane River's confluence with the Spokane River, is in a basin formed by crystalline basement rock that is filled with rocks and sediments of younger ages including basalt, clay, and sand. Seven important hydrogeologic units are recognized within the geologic framework in the study area. They are: (1) the crystalline basement aquifer, (2) the lower sand and gravel aquifers in the Latah and Pleistocene deposits, (3) aquitards composed of the clays of the Latah and Pleistocene deposits, (4) upper (surficial) sand and gravel aquifers, (5) landslide aquitards, (6) the Grande Ronde Basalt aquifers, and (7) the Wanapum Basalt Priest Rapids Member aquifers. Crystalline basement rocks with little weathering or fracturing act as the lower hydrogeologic boundary. Groundwater occurs in the weathered and fractured portions of the crystalline basement rock (Boese et al 1997).

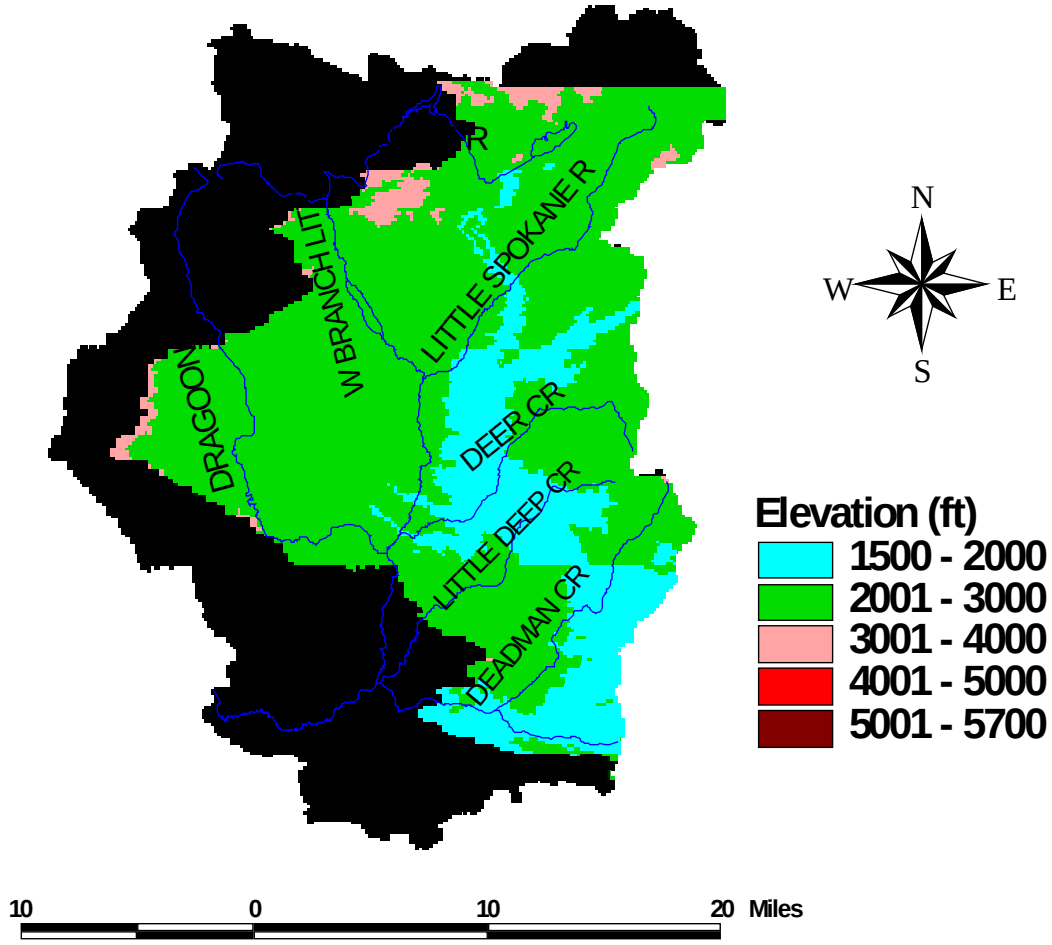


Figure 3. Elevation Ranges in Little Spokane Watershed

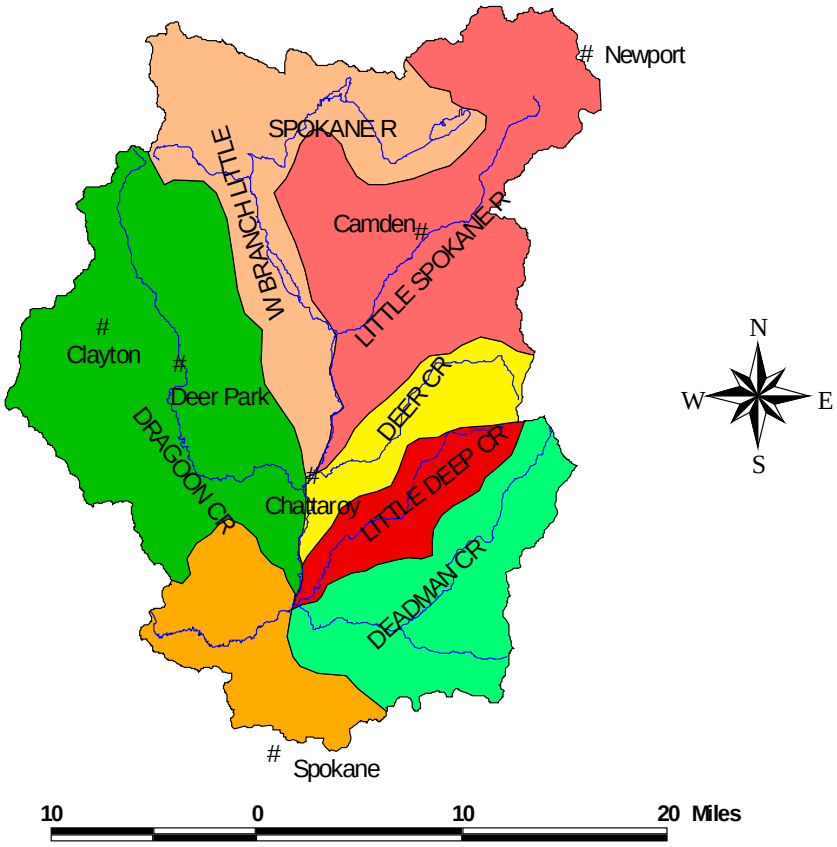


Figure 4. Seven Subbasins of Little Spokane Watershed

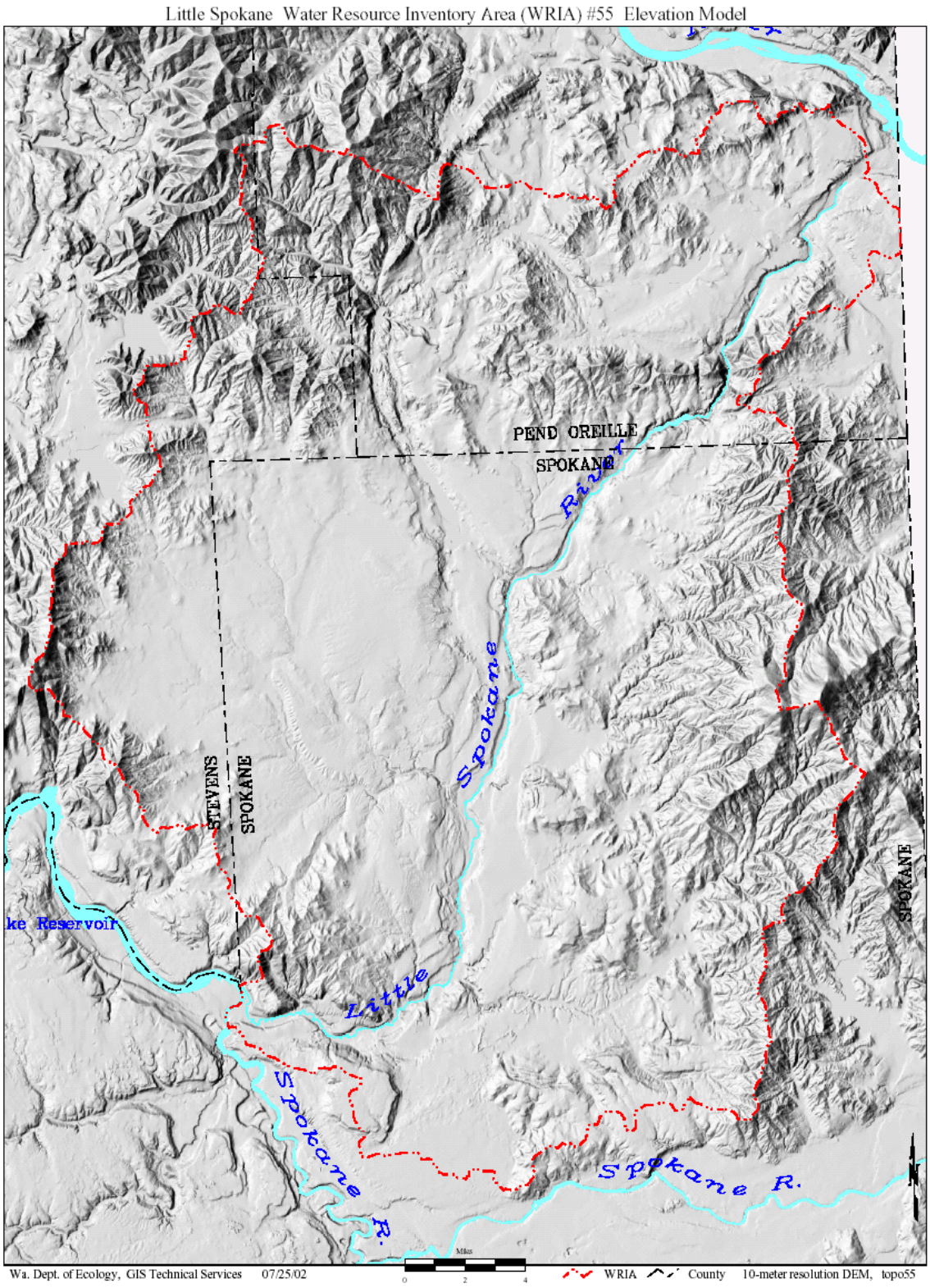


Figure 5. Digital Elevation Model of Little Spokane Watershed

2.3.4 Climate

The basin climate ranges from semiarid to subhumid, 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 is more than 44 inches per year. Figure 6 shows the precipitation distribution in the Little Spokane River Watershed. Table 1 shows the precipitation information measured at weather reporting stations at Deer Park, Mt. Spokane Summit, Newport, and the Spokane Weather Bureau at the Airport (WBAS). In addition to spatial variations, Table 1 indicates that there are considerable temporal variations in precipitation amounts. These 30-year averages compare reasonably well to the longer periods available at some stations. For example, the average annual precipitation at the Spokane Airport from January 1890 through July 2003 is 16.06 inches compared to the 16.70 inches determined from the last 30 years of record. The summer months of July, August, and September receive relatively little precipitation compared to the wetter winter months.

A significant amount of the winter precipitation occurs as snowfall, especially in the upper elevations such as the Mt. Spokane Summit. This can affect the timing of the runoff and associated nonpoint source pollutants. Occasional sudden warm winds or rains in winter can melt the snow rapidly. If this happens when the ground is frozen, the water runs off rapidly into the streams instead of soaking into the ground. This can lead to localized flooding and higher than normal sediment loads.

Average monthly temperature characteristics (maximum, mean, and minimum) for the four stations in or near the LSR are shown in Table 2. The mean monthly values are also presented in Figure 7. As shown, with the exception of the station on the summit of Mt. Spokane, the temperature data is fairly uniform across the basin. The elevation difference causes the Mt. Spokane station to be consistently 8-10 ^{o}F cooler than the other stations.

Frost penetrates 12 to 18 inches into the ground during a normal year, while during a cold winter it may penetrate as deep as 30 inches. The frost-free period ranges from 80 to 140 days depending on soil characteristics and climate; the frost-free period of the Eloika series is 80 days, that of the Clayton series which is predominant in Dragoon Creek Subbasin is 110 days, Green Bluff series – 135 days, Uhlig series on Pleasant Prairie – 140 days, and Phoebe series in the area of Wethey Creek and on Half Moon Prairie are about 140 days.

Table 1. Average monthly precipitation values for 1971-2000 (inches: http://www.wrcc.dri.edu/summary/climsmwa.html)

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

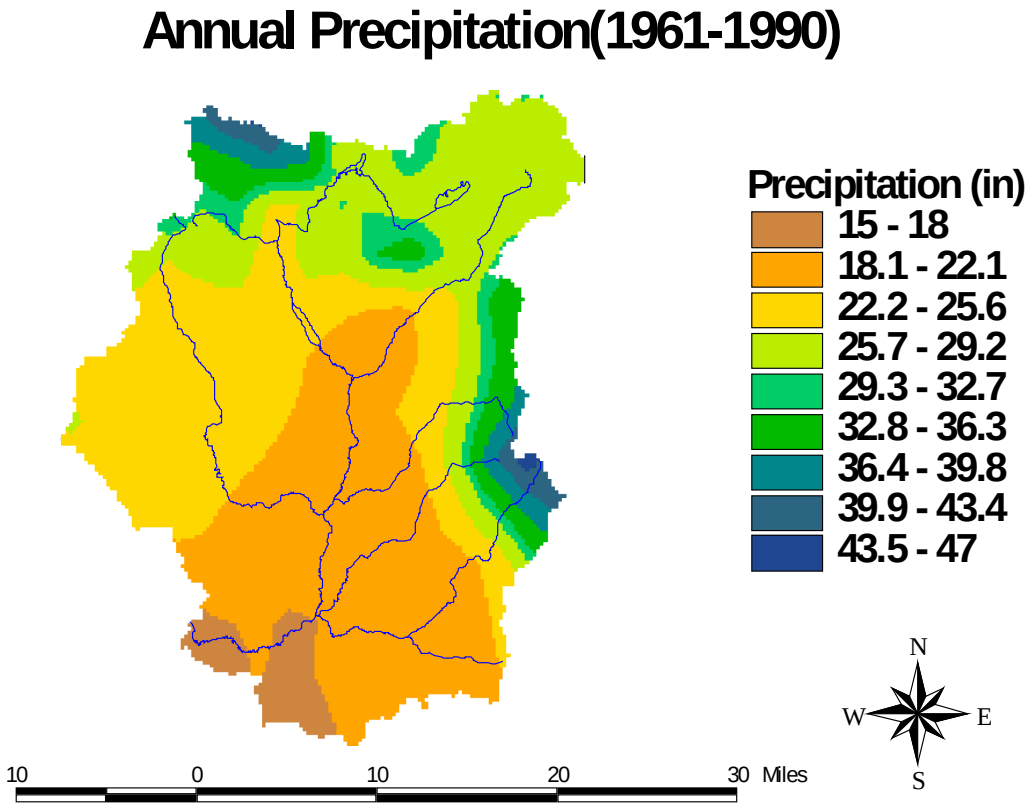


Figure 6. Precipitation Distribution within Little Spokane Watershed (inches/year)

Table 2. Temperature Summaries for Local Weather Stations (in degrees F)

Station Name		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Deer 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
	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
	Min	16.1	21.1	25.0	31.5	39.2	45.0	48.5	46.5	39.7	31.3	26.8	20.8
Mt. Spokane Summit	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
	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
	Min	13.1	18.4	19.4	24.9	35.0	41.1	49.3	48.8	40.9	30.8	22.5	16.9
Newport	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
	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
	Min	17.9	20.9	25.6	31.1	38.0	43.9	46.3	44.4	38.4	32.5	27.3	21.7
Spokane International 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
	Min	21.5	25.2	30.5	36.5	43.7	50.1	55.8	54.5	46.6	37.7	30.1	24.4

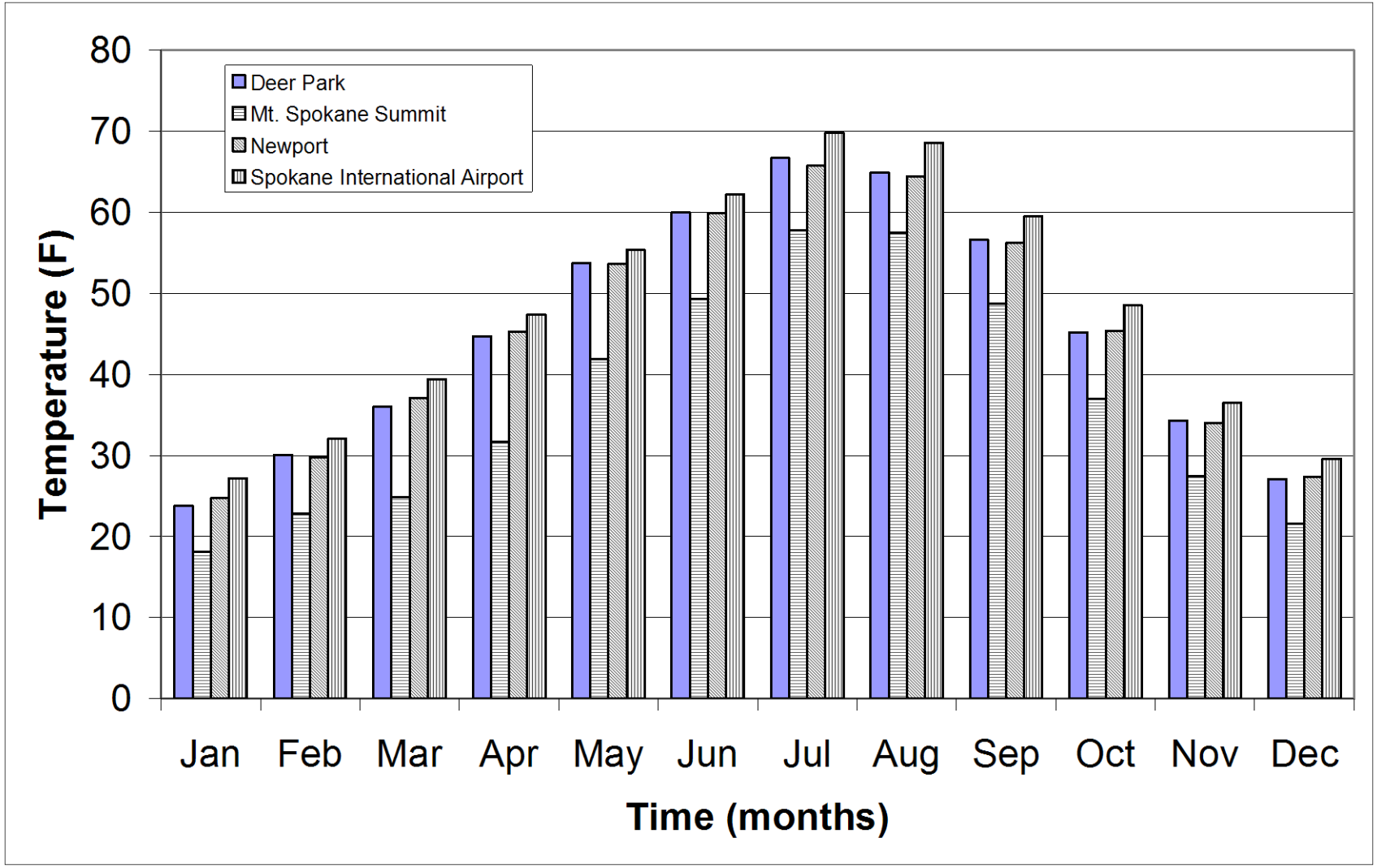


Figure 7. Average Monthly Temperatures in LSR Region (°F)

2.3.5 Land cover/Land use

The term “land cover” is used to describe the physical characteristic of land, such as mountains, water bodies, and soils. Land use is the manner in which humans use the land resources, such as forest, agriculture, industry, commercial, or road. Land use is a major way through which humans change the natural environment and is a main driving force of land cover change. Because there is a close relationship between land cover and land use, most references categorize them together as ‘land cover/land use’.

As illustrated in Figure 8, land uses in the Little Spokane River watershed vary greatly. Existing land cover is primarily forest interspersed with areas of rangeland, agriculture and development. Principal agricultural uses are fruit orchards, cultivated crops, and livestock rearing. Deer Park, Mead and the northern portion of Spokane are the main urban development areas. Two tables summarize the land use data calculated from GIS layers for the Little Spokane watershed: Table 3 reports the information separated by county; Table 4 summarizes the information by sub-watershed.

The results presented in Table 4 show that forested area is the predominant land cover/land use type in all of the watersheds. Figure 9 illustrates the land use/land cover distribution. The spatial distribution of land cover/land use show that the forestry areas are generally located in the northern and eastern portions of the watershed, the agriculture in the central, and resident in the southern.

Over the last decade, land use changes in the watershed have been dramatic, especially near the Spokane area. Economic growth has led to much of this area being converted from rural land to urban and suburban environments. Land use activities can significantly alter the quantity and quality of both surface and ground water moving through a watershed.

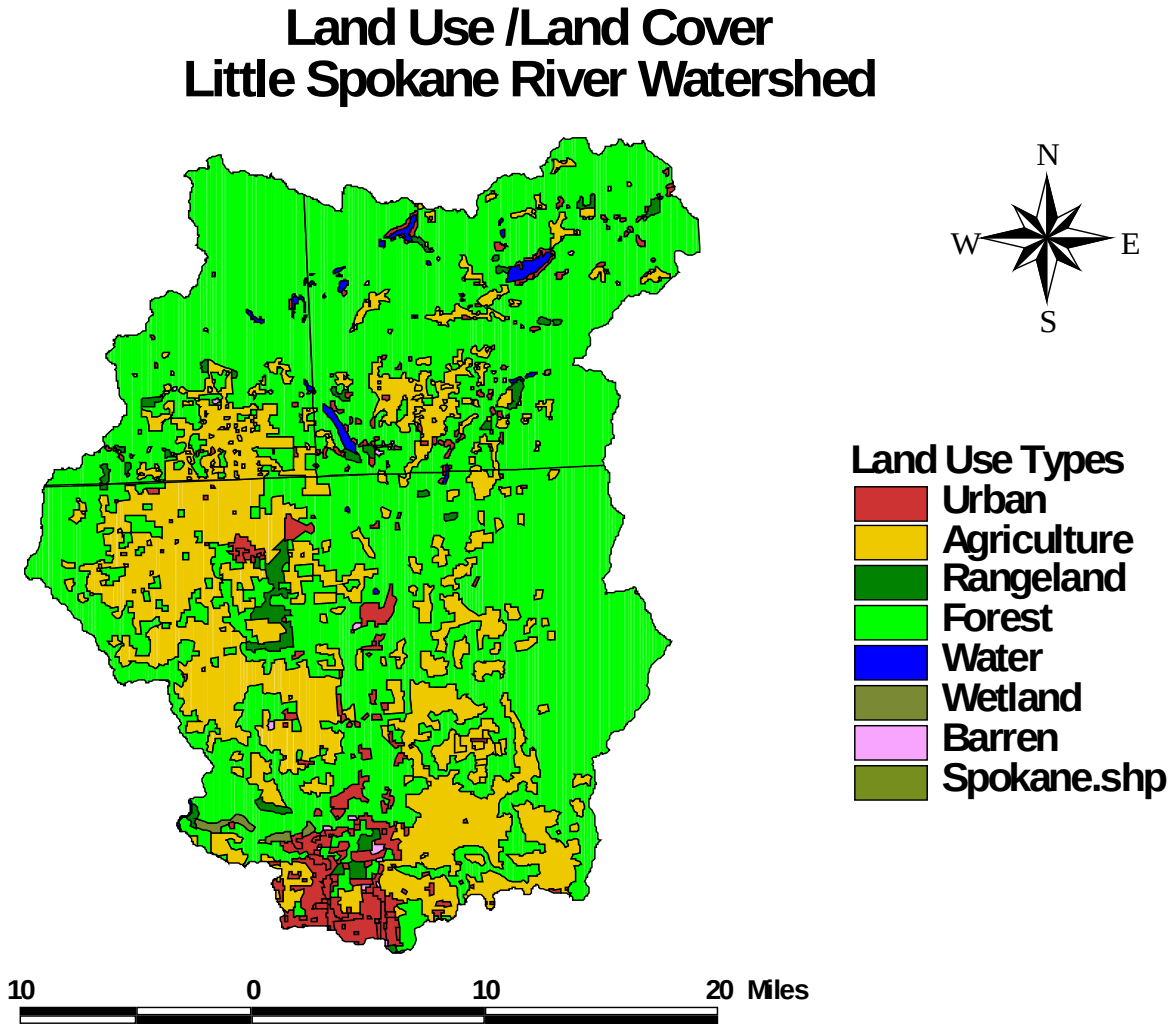


Figure 8. Land Cover/Land Use in the Little Spokane Drainage Basin

Table 3. Land Use acreages in Little Spokane Watershed (Pend Oreille Conservation District 2000)

Land Use	Spokane County	Pend Oreille County	Stevens County
Agriculture	76,293	11,368	18,141
Commercial	2,834	63	-
Cultural Recreational	681	565	-
Forestry	34,630	88,537	40,246
Government Services	13,228	156	-
Multiple Family Housing	1,713	-	-
Single Family Housing	52,069	1,258	-
Two Family Housing	2	-	-
Vacant	52,390	4,125	-
Industrial	1,822	-	-
Other or No Data	31,577	1,650	224

Table 4. Distribution of land use in the Little Spokane Watershed (percent)

Subbasin	Urban	Agriculture	Rangeland	Forest	Water	Wetland	Barren
Little Spokane (Downstream)	24.3	19.2	2.9	49.3	0.3	3.6	0.3
Dragoon Creek	1.9	47.3	2.7	47.9	0.0	0.0	0.1
West Branch	2.3	7.8	1.0	86.5	2.2	0.0	0.2
Little Spokane (Upstream)	2.2	13.7	1.8	81.7	0.4	0.1	0.1
Deer Creek	2.7	14.1	0.0	83.0	0.1	0.0	0.1
Little Deep Creek	8.1	35.4	1.1	54.9	0.0	0.0	0.5
Deadman Creek	3.1	27.0	0.0	69.9	0.0	0.0	0.0

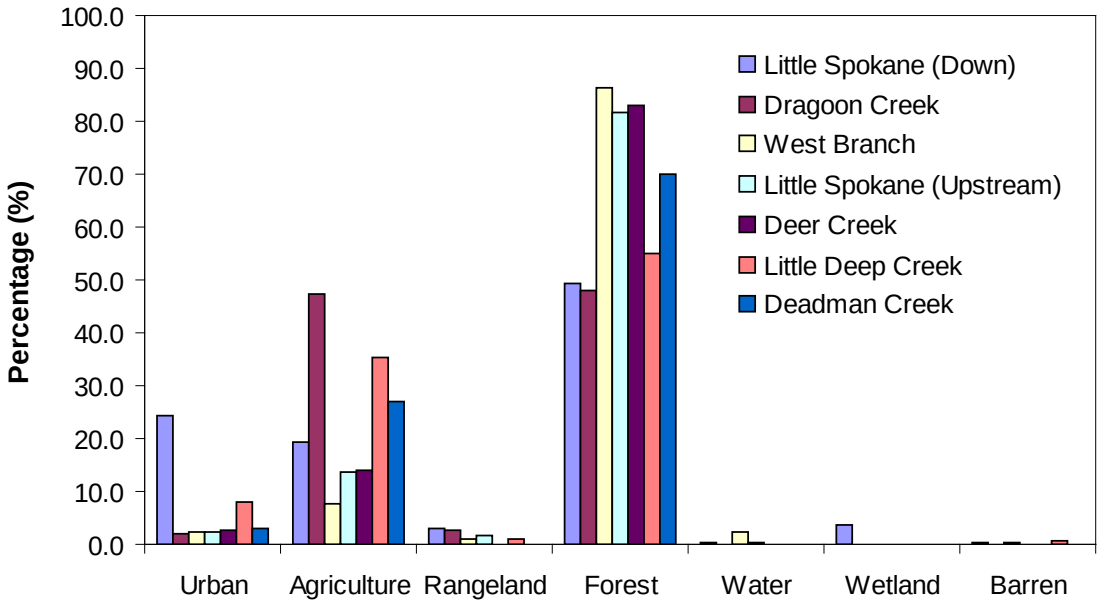


Figure 9. Percentage distribution of land use in the Little Spokane Watershed

3 WATER RESOURCES

3.1 Surface Water Resources

With high mountains on the north and the 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 months, 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.

Surface water in the watershed includes numerous rivers, streams, and lakes. The major tributaries to the Little Spokane River are Dragoon, Deadman, Little Deep and Deer creeks as well as the West Branch of the Little Spokane River. The largest lakes include Eloika, Diamond, Sacheen and Horseshoe lakes, which are all located in the northern half of the watershed.

In spite of the quantity of surface water, relatively little water is directly diverted for public consumption. A 1990 USGS survey found that the 5.65 million gallons per day (MGD) of surface water diverted was used to water a portion of the 9,400 acres of irrigated agriculture (USGS, 1990). The total consumptive use in the Little Spokane basin is presented in Table 5. As indicated, the municipal/domestic use category consumes the majority of water in the watershed presumably due to lawn watering and residential gardening/landscaping.

Table 5. Summary of Estimated Consumptive Use for the Little Spokane Watershed (USGS, http://water.usgs.gov/cgi-bin/wuhuc?huc=17010308)

Purpose of Use	Actual Use (AF/yr)	Irrigation Use (%)	Irrigation Use (AF/yr)
Agricultural Irrigation	6,398	100%	6,398
Municipal/Domestic	24,553	50%-60%	12,276-16,369
Commercial/ Domestic	3,929	Unknown	-
Exempt Wells	11,000	50%-67%	5,500-7,333

As summarized in Table 6, three USGS streamflow gaging stations have been historically operated in the Little Spokane watershed. Currently, only the station at Dartford (12431000) is in operation. This gage has been in continuous operation for over 54 years resulting in an excellent long-term period of record.

Table 6. Summary of USGS gaging stations

Gage Number	Location	Basin Area (square miles)	Operation	Years of Data
12427000	Little Spokane River at Elk	117	07/01/48 10/22/71	23
12431000	Little Spokane River at Dartford	665	05/01/29 09/30/32 10/01/47 09/30/02	3 54
12431500	Little Spokane River near Dartford	698	04/01/48 03/31/52 10/01/97 09/30/02	4 5

Figure 10 illustrates the average monthly flow at the two stations located on the lower Little Spokane River in the vicinity of Dartford, WA. The upstream gage (12431000) is located at River Mile (RM) 11.4 while the downstream gage (12431500) is located at RM 3.8 (this station was discontinued in 2002). The pattern of runoff is consistent with typical snowmelt watersheds with peak discharges occurring in April followed by dramatic decreases in streamflow during the late summer months of August and September.

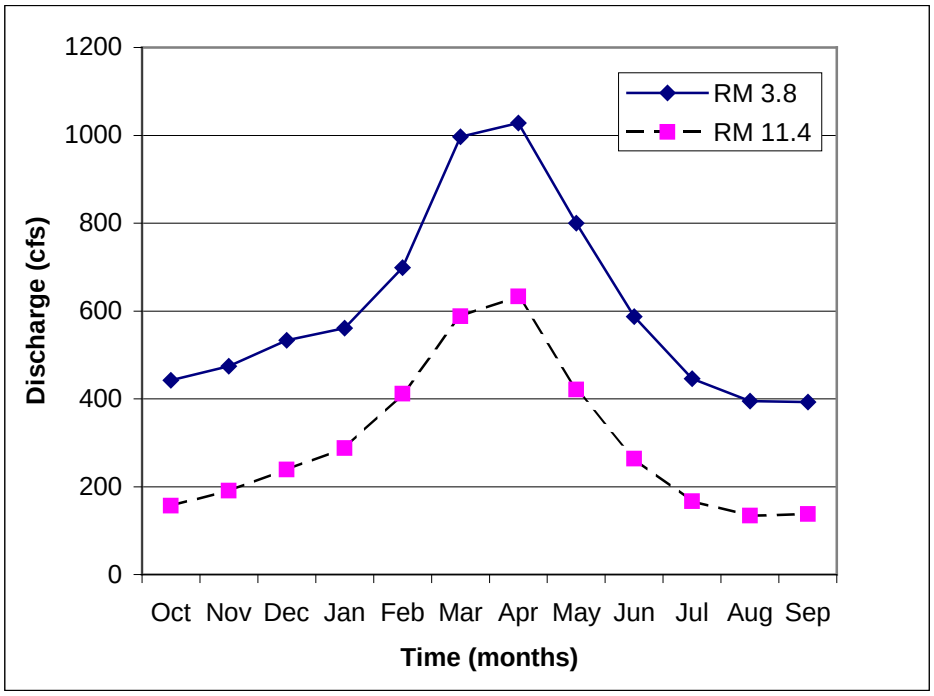


Figure 10. Average monthly discharge on Little Spokane River (USGS gage 12431500 – RM 3.8 and 12431000 – RM 11.4, WY 1997-2002)

The Spokane County Conservation District (SCCD) has operated five continuous stream gages in the watershed since September 1999. The stations monitor stream stage hourly and are situated on the following streams:

LS-1 Little Spokane River, Scotia Rd. near Newport
LS-3 Otter Creek, Elk to Highway Rd. near Elk
LS-4 Little Spokane River, Deer Park-Milan Rd. near Riverside
LS-5 Dragoon Creek, Crescent Rd. at Chattaroy
LS-6 Deadman Creek, 15628 N. Little Spokane Drive in Spokane

Instantaneous flow measurements have been recorded at other locations. Ecology has a water quality monitoring station (55B070) near the mouth of the Little Spokane (RM 1.5). The flow is recorded each month that water quality samples are taken.

3.2 Ground Water Resources

Part of the precipitation on the surface soaks into the ground and moves downward to the zone of saturation, where it becomes part of the Little Spokane River ground water reservoir. This in turn is discharged into the mainstem of the Little Spokane River when flow levels are low. The majority of natural ground water discharge in the watershed occurs as baseflow to the Little Spokane River. In low flow periods (especially during August and September), flows at Dartford, WA total approximately 150 cfs and consist primarily of ground water inflows (Chung, 1975). During summer drought periods, entire discharge in the mainstem of the river is contributed by ground water baseflow. The east branch of the Little Spokane River upstream of the confluence with the west branch makes its discharge through ground water flow (Chung, 1975).

Ground water supplies most of the domestic drinking water in this watershed. The Spokane Valley Rathdrum Prairie (SVRP) aquifer, the Deer Park ground water basin and the Little Spokane aquifer are the three most important aquifers within WRIA 55. The Green Bluff, Peone Prairie, Orchard Prairie and Five Mile Prairie aquifers provide considerably less water, but are nevertheless important locally. Brief discussions of these aquifers are provided below:

The SVRP covers an area of about 320 square miles, 200 square miles of which lies within Idaho and 120 square miles of lies within Washington. The SVRP extends from the western end of Lake Pend Oreille and from the arm of Lake Coeur d'Alene in Idaho, westwards and southwards beneath the Rathdrum Prairie and westwards down the Spokane river valley. The principal sources of recharge to the SVRP aquifer are groundwater inflow from Idaho, direct infiltration of precipitation and irrigation water, seepage from lakes along the perimeter of the aquifer, surface waters that originate in the surroundings uplands and flow onto and infiltrate into the aquifer, and recharge from Spokane River.

The lower reach of the river, beginning approximately four miles below Dartford and extending downstream to the mouth, obtains a significant amount of ground water discharge from the

Spokane Valley/Rathdrum Prairie (SVRP) aquifer (Molenaar, 1988). While the SVRP aquifer is present only in the southern portion of the Little Spokane watershed, it is very important to the region as it provides majority of potable water for the Spokane metropolitan area. Wells within the Spokane-Rathdrum aquifer can be expected to yield in the hundreds to thousands of gallons per minute.

The Deer Park ground water basin is located in the central and eastern portions of WRIA 55. It consists of a shallow aquifer within the unconsolidated sediments and a deeper aquifer system that is contained within the basalts, Latah sediments and crystalline basement rocks (Golder 2003). In general, ground water in the unconsolidated sediments flows from northwest to the southwest across the basin, discharging into the Little Spokane River to the east and Dragoon Creek to the south.

The Little Spokane River aquifer is located within WRIA 55 and covers the area south and east of the Deer Park groundwater basin and north of the Little Spokane River and the SVRP aquifer. The aquifer materials are comprised of unconsolidated sediments that range locally up to 400 feet. Although very little amount of information is available on ground water flow, elevation, and direction, it is likely that ground water within the aquifer is flowing in major streams such as Dartford Creek, Deadman Creek, and Little Spokane River.

Diamond Lake aquifer is located within Pend Oreille County. This aquifer is made up of sedimentary deposit located in the vicinity of Diamond Lake and includes sediments of Diamond Lake basin and Scotia Valley. The ground water flow direction is from the Pend Oreille River Watershed into WRIA 55 in a southwesterly direction through the sediments of Diamond Lake Basin and Scotia Valley.

Green Bluff aquifer is four square miles topographic high located in WRIA 55, within the northeastern extent of the Columbia River Plateau. The Green Bluff Aquifer occurs within the basalt and is unconfined.

The Orchard Prairie aquifer has limited ground water resources and recharge primarily occurs through precipitation (Golder 1990; 2003).

The Five Mile Prairie aquifer is a four square mile topographic high located within partially in WRIA 55, WRIA 56 and WRIA 57. The geology of this aquifer is comprised of loess, Wanapum Basalt, Latah sediments and Grande Ronde Basalt. Ground water occurs as both unconfined and confined aquifers within the basalt flows.

Finally, the Peone Prairie aquifer is located in WRIA 55 and has limited ground water resources (Spokane County 1996) and precipitation is the main source of recharge.

3.3 Surface/Ground Water Interaction

Surface/Ground water interaction is an important feature in the lower portion of the Little Spokane watershed. Examining the average annual hydrographs shown in

Figure 10 reveals that while the shapes of the two curves is nearly identical, there is substantially more flow at the downstream gage. Although the contributing area increases by only 5 percent, the average discharge increases rather appreciably and relatively uniformly. The gage at Dartford (RM 11.4) is upstream of Dartford Creek but this single small drainage area cannot explain the large increase in flow. All other significant surface water tributaries are located upstream of both gages. In order to rule out the possible influence of differences in the gaging periods, daily flow data was downloaded for the five years of overlapping record (1997-2002). The resultant information is shown in Figure 11. As indicated, the difference between the two gages remained significant. Comparison of the two gages indicated that, on average, the downstream gage gained approximately 250 cfs. Moreover, the standard deviation was a modest 35 cfs. Interpretation of this data leads to the conclusion that significant ground water inflows from the Spokane Valley-Rathdrum Prairie aquifer and other sources must be feeding seeps, springs and hyporheic zone contributions to the stream flow. While the SVRP contributes the majority of the water, up to one quarter of it may be the result of discharge from ground water originating in the upper portion of the Little Spokane River (Cline, 1969). Such flows may help mitigate summer temperatures; however, they may in fact be detrimental to dissolved oxygen levels particularly near the stream bed.

Despite the seasonal closure of consumptive appropriation in the Little Spokane River Watershed since 1980 (WAC 173-555), minimum base flows have continued to decline due to the rapid increase in domestic water use via ground water pumping (Whalen 2000).

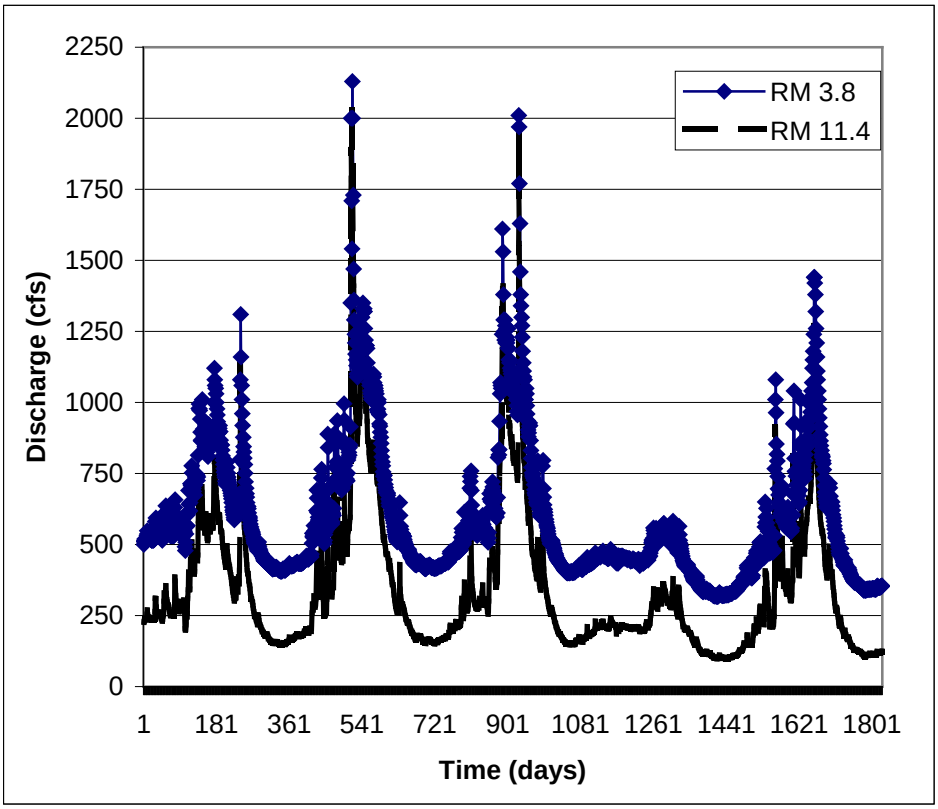


Figure 11. Average Daily Discharges from 10/1/97 to 9/30/02 from USGS stations

3.4 Surface Water Quality Issues

Ecology has identified the Little Spokane River as a water body with water quality and water quantity issues. Since the wastewater treatment plant at Deer Park now uses land applications for treating its summer discharge, no specific point sources have been identified that contribute to the water quality problems in the Little Spokane River (Ecology 1992). Nonpoint sources are the main contributors to pollution problems in the Little Spokane River. A majority of the land in the Little Spokane watershed is used for agricultural purposes. Runoff of pesticides and fertilizers from agriculture practices are potential nonpoint source pollutants. Dairies located around the basin also contribute to the water quality problems. There are about 14 dairies in Spokane County with a total animal number of 2,677. We did not find any specific references of dairies in Pend Oreille County. Grazing by cattle and cattle having access to the river have also exacerbated the problem. Temperature problems appear to be the result of both natural and anthropogenic causes. Increased ground water pumping has reduced base flow in certain sections of the watershed thus exasperating the stream temperature problem. Water discharge permits for the Little Spokane River are given in Table 7.

The lower portion of the watershed, especially in the Spokane area, has seen a lot of land use changes due to urbanization. Because of rapid economic growth in North Spokane, much of the rural land has been converted to urban and suburban environments (Dames and Moore 1995). Such increases in housing and commercial development have given rise to nonpoint source pollutants such as septic systems, urban/highway storm water, and agricultural runoff. Forest practices related to timber harvesting have also contributed to this problem.

Other potential problems that were seen in the Little Spokane River in 1992 when a statewide wide water quality assessment was carried out included (Ecology, 1995):

- The Little Spokane River (48.6 miles) was not meeting swimmable and fishable goals of the federal Clean Water Act and water quality standards for priority pollutants. Causes included metals (cyanide and mercury), inorganics, and pathogens indicators such as fecal coliform. Sources included agriculture, landfills, hazardous waste disposal sites and inplace contaminants.

- Diamond Lake was considered threatened for supported beneficial uses due to nutrient levels. Causes included land development, sludge, removal of riparian vegetation and natural sources.

- Eloika Lake was considered as having impaired aesthetic enjoyment due to nutrients, siltation, and taste odor. The sources were unknown.

- Sacheen Lake was considered impaired for aesthetic enjoyment due to eutrophication. No cases of sources were identified.

Table 7. NPDES Permits in the Little Spokane River (Turner, 2004)

Type	Size	City	County	Permit No.	Expiration Date	Permit Status
FARM	GENERAL PERMITS	DEER PARK	SPOKANE	WAG017002A	2-Sep-99	A
INDUSTRIAL	GENERAL PERMITS	ELK	SPOKANE	WAG507067B	6-Aug-04	A
INDUSTRIAL	GENERAL PERMITS	SPOKANE	SPOKANE	WAG507074B	6-Aug-04	A
MUNICIPAL	STATE TO GROUND	LOON LAKE	STEVENS	ST0005392B	30-Jun-07	A
MUNICIPAL	STATE TO GROUND	DEER PARK	SPOKANE	ST0008016C	30-Jun-07	Z
MUNICIPAL	STATE TO GROUND	NEWPORT	PEND OREILLE	ST0008029D	9-Apr-07	A
FARM	GENERAL PERMITS	CHATTAROY	SPOKANE	WAG017001A	2-Sep-99	A
INDUSTRIAL	GENERAL PERMITS	DEER PARK	SPOKANE	WAG507022B	6-Aug-04	A
FISH	GENERAL PERMITS	SPOKANE	SPOKANE	WAG137007C	1-Jun-05	A
INDUSTRIAL	GENERAL PERMITS	ELK	SPOKANE	WAG507027B	6-Aug-04	A
INDUSTRIAL	GENERAL PERMITS	CHATTAROY	SPOKANE	WAG507008B	6-Aug-04	A
INDUSTRIAL	GENERAL PERMITS	CHATTAROY	SPOKANE	WAG507065B	6-Aug-04	A
INDUSTRIAL	GENERAL PERMITS	ELK	SPOKANE	WAG507095B	6-Aug-04	A

Milfoil that has infested lakes such as Diamond Lake, Sacheen Lake, Fan Lake, and Eloika Lake poses a concern for the water quality of the Little Spokane River basin (POCD, 1998). Although Milfoil has been restricted to the lakes, the stream channel remains prone to the invasion by Milfoil. Along the Little Spokane River channel, milfoil has been found at two sites: at Harworth Road approximately one mile below Sacheen Lake and at Eloika Road, approximately 0.2 miles below Eloika Lake. Milfoil, due to its invasive nature, alters the aquatic habitat and interferes with recreation activities such as swimming, fishing and boating. Chemical measures have been taken to combat this problem at the lakes. The chemicals used could also be affecting the river at downstream. However, no study has been done to locate these downstream effects.

Permits have recently been given to apply 2, 4_D in Sacheen Lake and Diamond Lake to control Milfoil. At present no measures are being taken to control milfoil in Bear Lake, Chain Lake, Eloika Lake, Trout Lake, and Horshoe Lake. The herbicide application is done only once in summer, generally starting from June to August and does not go beyond October. The application time depends on the weather as well as on the density of milfoil (Hamel, 2004).

Golder (2003) conducted the most recent survey of water quality in WRIA 55 in a comprehensive report to Spokane County and the local Planning Unit. Their report essentially supported earlier findings that dissolved oxygen, fecal coliform, pH, temperature, and PCBs are still the primary pollutants of concern. DO and temperature problems were most likely to occur during summer months coinciding with low flow periods. Fecal coliform concentrations were quite variable throughout the year with some dilution effects during the spring freshet. The pH values were also variable however, unlike the fecal coliform data, no significant correlation to flow was observed.

As a result of these water quality problems, Ecology identified the Little Spokane River as an impaired Washington state waterway. The Little Spokane River was put on 303(d) list in 1998 and 2002/2004 for violation of state's water quality standards (Appendix A) for pH, temperature, dissolved oxygen, fecal coliform, and PCBs. The water segments in violation of the water quality standards in 1998 and 2002/2004 are summarized in Table 8 and Table 9, respectively. The locations of the 1998 violations are shown in Figure 12. The locations of the 2002/2004 violations are shown in Figure 13.

The proposed 2002/2004 303(d) list includes 5 categories of stream segments. Table 10 summarizes the different stream classifications now used. Category 1 identifies the stream segments that have been sampled and found to meet existing standards. Forty-two of the entries in Table 9 are for stream segments that are known to meet these standards. An additional twenty-three segments are listed as areas of concern (Category 2); meaning that either data are insufficient to support listings or that recent trends seem to indicate future problems.

Table 8. 1998 303 (d) List for Little Spokane River

Id #	Name	Segment #	Parameter
192	Deadman Creek	MY92TJ	Temperature
192	Deadman Creek	MY92TJ	pH
193	Dragoon Creek	GL94EJ	Dissolved oxygen
194	Dragoon Creek	GL94EJ	Dissolved oxygen
194	Dragoon Creek	GL94EJ	Fecal Coliform
195	L. Spokane River	JZ07CP	PCB-1248(t)
195	L. Spokane River	JZ07CP	PCB-1254(t)
195	L. Spokane River	JZ07CP	PCB-1260(t)
196	L. Spokane River	JZ07CP	Fecal Coliform
197	L. Spokane River	JZ07CP	Fecal Coliform
197	L. Spokane River	JZ07CP	Temperature
197	L. Spokane River	JZ07CP	pH
198	L. Spokane River	JZ07CP	Temperature
199	Dragoon Creek	ST18TI	Dissolved Oxygen

Table 9. 303 (d) List for Little Spokane River for 2002/2004

Listing ID	Cat	WRIA	Waterbody Name	Parameter	Medium	Twp	Rg	Sec
16854	5	55	DEADMAN CREEK	Fecal Coliform	Water	27N	43E	33
16856	5	55	DRAGOON CREEK	Fecal Coliform	Water	28N	43E	33
9051	5	55	LITTLE SPOKANE RIVER	Total PCBs	Tissue	26N	42E	4
15924	5	55	LITTLE SPOKANE RIVER	Turbidity	Water	26N	43E	6
6325	5	55	SACHEEN LAKE	Fecal Coliform	Water	31N	43E	35
6367	5	55	SACHEEN LAKE	Total Phosphorus	Water	31N	43E	35
5378	4C	55	DEADMAN CREEK	Fish Passage Barrier	Habitat	28N	45E	28
5377	4C	55	DEADMAN CREEK	Fish Passage Barrier	Habitat	28N	45E	33
4884	4C	55	DIAMOND LAKE	INVASIVE EXOTIC SPECIES	Habitat	30N	44E	3
4885	4C	55	ELOIKA LAKE	INVASIVE EXOTIC SPECIES	Habitat	29N	43E	15
4886	4C	55	FAN LAKE	INVASIVE EXOTIC SPECIES	Habitat	30N	43E	32
10492	4C	55	HORSESHOE LAKE	INVASIVE EXOTIC SPECIES	Habitat	30N	43E	8
4887	4C	55	LITTLE SPOKANE RIVER	INVASIVE EXOTIC SPECIES	Habitat	31N	45E	34
4888	4C	55	SACHEEN LAKE	INVASIVE EXOTIC SPECIES	Habitat	31N	43E	35
9049	4A	55	DRAGOON CREEK	Ammonia-N	Water	28N	42E	3
9050	4A	55	DRAGOON CREEK	Chlorine	Water	28N	42E	3
9048	4A	55	DRAGOON CREEK	Total Phosphorus	Water	28N	42E	3
23091	2	55	BEAR (KUESTER) LAKE	Total Phosphorus	Water	28N	43E	15
23092	2	55	CHAIN LAKE	Total Phosphorus	Water	28N	06E	24
9054	2	55	DEADMAN CREEK	Aluminum	Water	26N	43E	3
11388	2	55	DEADMAN CREEK	pH	Water	27N	43E	33
11387	2	55	DEADMAN CREEK	Temperature	Water	27N	43E	33
8445	2	55	DRAGOON CREEK	Dissolved oxygen	Water	29N	42E	8
8444	2	55	DRAGOON CREEK	Dissolved oxygen	Water	30N	42E	18
8443	2	55	DRAGOON CREEK	Dissolved oxygen	Water	28N	42E	3
8446	2	55	DRAGOON CREEK	Fecal Coliform	Water	30N	42E	18
8442	2	55	DRAGOON CREEK	Fecal Coliform	Water	29N	42E	8
11370	2	55	DRAGOON CREEK	pH	Water	28N	43E	33
11371	2	55	DRAGOON CREEK	Temperature	Water	28N	43E	33
23093	2	55	ELOIKA LAKE	Total Phosphorus	Water			
6334	2	55	ELOIKA LAKE	Total Phosphorus	Water	29N	43E	15
23094	2	55	FAN LAKE	Total Phosphorus	Water			

Table 9. 303 (d) List for Little Spokane River for 2002/2004 (continued)

11374	2	55	LITTLE SPOKANE RIVER	Dissolved oxygen	Water	26N	42E	5
16857	2	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	28N	43E	27
11373	2	55	LITTLE SPOKANE RIVER	pH	Water	26N	42E	5
11380	2	55	LITTLE SPOKANE RIVER	Temperature	Water	27N	43E	33
11384	2	55	LITTLE SPOKANE RIVER	Temperature	Water	28N	43E	27
3735	2	55	LITTLE SPOKANE RIVER	Temperature	Water	26N	42E	5
23095	2	55	REFLECTION LAKE	Total Phosphorus	Water			
23096	2	55	TROUT LAKE	Total Phosphorus	Water	25N	12E	31
11386	1	55	DEADMAN CREEK	Ammonia-N	Water	27N	43E	33
11385	1	55	DEADMAN CREEK	Dissolved oxygen	Water	27N	43E	33
11366	1	55	DEER CREEK	Dissolved oxygen	Water	28N	43E	34
16855	1	55	DEER CREEK	Fecal Coliform	Water	28N	43E	34
11367	1	55	DEER CREEK	pH	Water	28N	43E	34
11365	1	55	DEER CREEK	Temperature	Water	28N	43E	34
22518	1	55	DIAMOND LAKE	Total Phosphorus	Water	30N	44E	3
11369	1	55	DRAGOON CREEK	Ammonia-N	Water	28N	43E	33
11368	1	55	DRAGOON CREEK	Dissolved oxygen	Water	28N	43E	33
6137	1	55	HORSESHOE LAKE	Fecal Coliform	Water	36N	01W	33
11379	1	55	LITTLE SPOKANE RIVER	Ammonia-N	Water	27N	43E	33
11383	1	55	LITTLE SPOKANE RIVER	Ammonia-N	Water	28N	43E	27
11376	1	55	LITTLE SPOKANE RIVER	Ammonia-N	Water	26N	43E	6
11375	1	55	LITTLE SPOKANE RIVER	Ammonia-N	Water	26N	42E	3
11372	1	55	LITTLE SPOKANE RIVER	Ammonia-N	Water	26N	42E	5
11377	1	55	LITTLE SPOKANE RIVER	Dissolved oxygen	Water	27N	43E	33
11381	1	55	LITTLE SPOKANE RIVER	Dissolved oxygen	Water	28N	43E	27
40880	1	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	27N	43E	33
16860	1	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	27N	43E	33
16859	1	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	26N	43E	6
16858	1	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	26N	42E	3
16861	1	55	LITTLE SPOKANE RIVER	Fecal Coliform	Water	26N	42E	5
11378	1	55	LITTLE SPOKANE RIVER	pH	Water	27N	43E	33
11382	1	55	LITTLE SPOKANE RIVER	pH	Water	28N	43E	27
22519	1	55	SACHEEN LAKE	Total Phosphorus	Water	31N	43E	35
23507	1	55	SPOKANE RIVER	Arsenic	Sediment	26N	42E	5

Table 9. 303 (d) List for Little Spokane River for 2002/2004 (continued)

23508	1	55	SPOKANE RIVER	BENZO(A)ANTHRACENE	Sediment	26N	42E	5
23509	1	55	SPOKANE RIVER	Benzo(g,h,i)perylene	Sediment	26N	42E	5
23510	1	55	SPOKANE RIVER	Chromium	Sediment	26N	42E	5
23511	1	55	SPOKANE RIVER	Chrysene	Sediment	26N	42E	5
23512	1	55	SPOKANE RIVER	Copper	Sediment	26N	42E	5
23513	1	55	SPOKANE RIVER	Dibenzofuran	Sediment	26N	42E	5
23514	1	55	SPOKANE RIVER	Fluoranthene	Sediment	26N	42E	5
23515	1	55	SPOKANE RIVER	HPAH	Sediment	26N	42E	5
23516	1	55	SPOKANE RIVER	Indeno(1,2,3-cd)pyrene	Sediment	26N	42E	5
23517	1	55	SPOKANE RIVER	LPAH	Sediment	26N	42E	5
23518	1	55	SPOKANE RIVER	Nickel	Sediment	26N	42E	5
23519	1	55	SPOKANE RIVER	Phenanthrene	Sediment	26N	42E	5
23520	1	55	SPOKANE RIVER	Phenol	Sediment	26N	42E	5
23521	1	55	SPOKANE RIVER	Pyrene	Sediment	26N	42E	5
23522	1	55	SPOKANE RIVER	Total Organic Carbon	Sediment	26N	42E	5
23523	1	55	SPOKANE RIVER	Zinc	Sediment	26N	42E	5

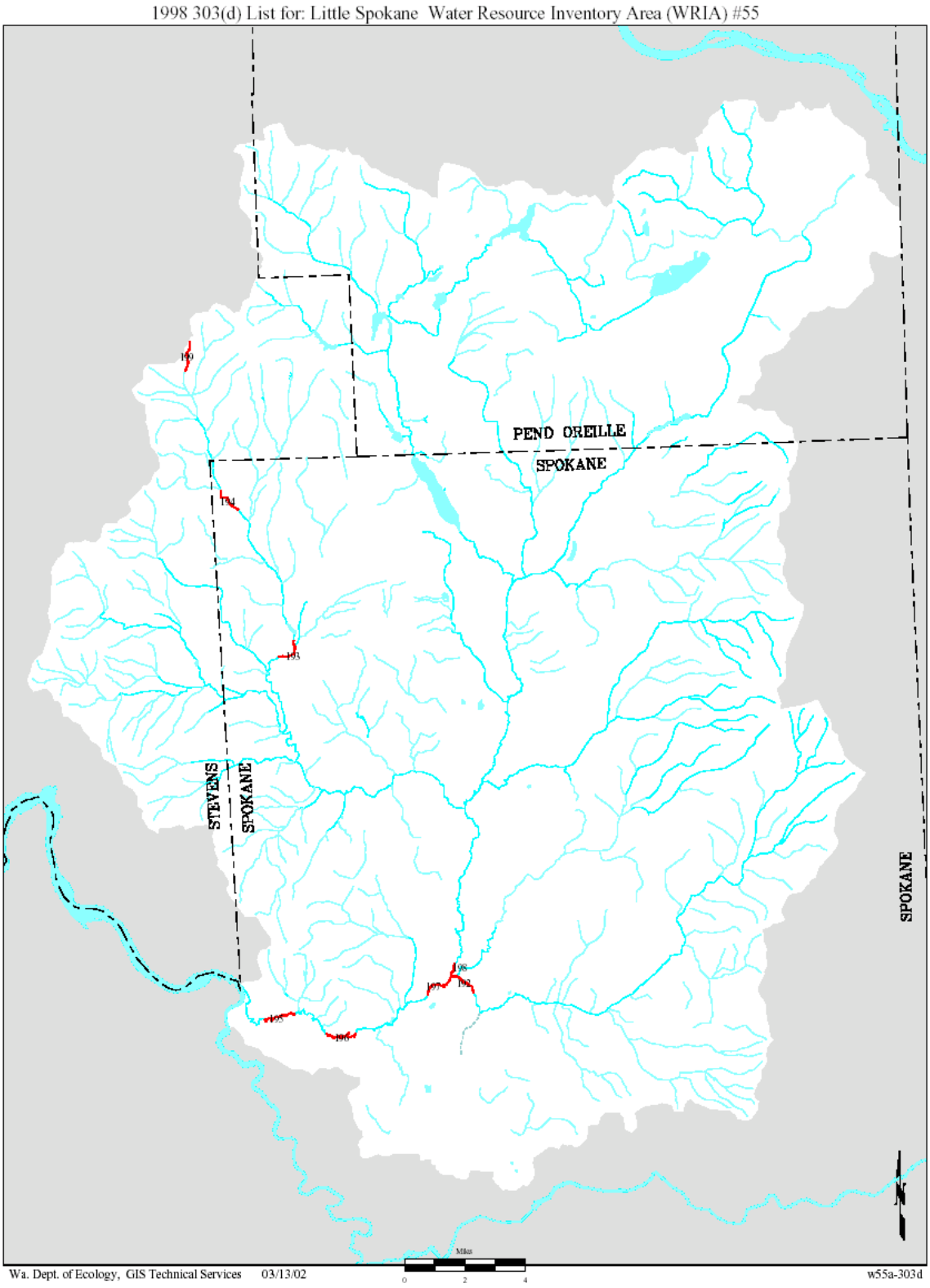


Figure 12. Locations of the stream segments on the 1998 303(d) list

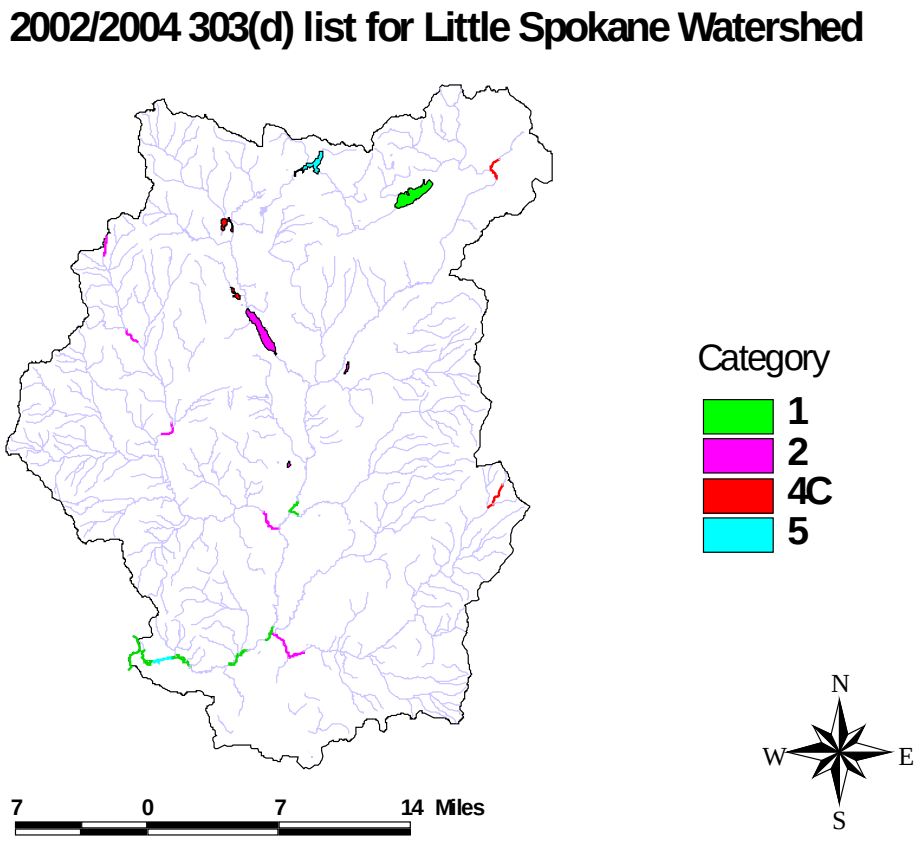


Figure 13. 2002/ 2004 303(d) list for Little Spokane Watershed

Table 10. Ecology Procedure for Categorizing Water Bodies

Classification	Condition
Category 1	Waters that meet current standards
Category 2	Waters of concern
Category 3	Waters with no data available
Category 4	Impaired waters but one of the following exits: Category 4A: Water has a TMDL Category 4B: Water has a pollution control plan Category 4C: Water is impaired by a non-pollutant
Category 5	On the 303(d) list

3.5 Ground Water Quantity/Quality Issues

Ground water use in WRIA 55 exceeds surface water use, drawing heavily from aquifers which are hydraulically connected with the Little Spokane River and its tributaries. The excessive ground water pumping has resulted in decrease in streamflow. This is especially the case in the western and southern portion of the watershed where ground water use is the greatest.

Since 1980's Ecology has monitored water levels in the Green Bluff Area (northeast of Spokane in township 27N Range 44E). Ground water in this area discharges to Deadman Creek and Little Deep Creek. Ground water level monitoring data from 1980-1990 indicates the ground water level has been declining due to excessive pumping of water for industrialization and irrigation purposes (Ecology, 1995).

Boese et al (1997) conducted a reconnaissance level sampling of 44 water wells in the Spokane County portion of the Little Spokane River watershed from April 23 to June 4, 1996. The data gathered in this study indicated the water quality of the wells tested was good except for high concentrations of iron. The major source of iron in groundwater in this area is basalt. Iron concentrations ranged from <0.010 to 14.9 mg/L with a mean concentration of 2.37 mg/L. Nitrogen values, measured as nitrate + nitrite concentrations, ranged from <0.01 to 9.86 mg/L with a mean concentration of 1.20 mg/L. The pH values ranged from 6.51 to 8.18 with a mean value of 7.35. The total hardness as CaCO3 concentration values ranged from <1 to 497.5 mg/L with a mean of 188.8 mg/L. The chloride concentration values ranged from 1.06 to 234.68 mg/L with a mean value of 9.50 mg/L. The specific conductance values ranged from 196 to 1163 µmhos/cm with a mean value of 373 µmhos/cm.

A study carried out by the Spokane County Conservation District in 2001-2002 indicated that ground water has been contaminated with nitrate near the Deadman Creek and Little Deep Creek. The source of nitrogen was from housing development as well as from the springs that are located around the Deadman Creek. The results of the SCCD study are summarized in Table 11 and Table 12. Although the nitrate level was high in both the areas, they did not exceed the US EPA recommended drinking water limit of 10 mg/L.

Table 11. Deadman Creek Nitrate and Nitrite Summary

Parameter (mg/l as N)		Deadman at Bruce Road	Deadman upstream of outfall and springs	Spring upstream of Kaiser outfall	Kaiser outfall	Spring upstream of Hwy. 2	Deadman at Shady Slope Road
Nitrate NO_3	Mean	0.14	0.53	1.70	1.47	3.09	0.82
	Maximum	0.23	0.98	1.74	1.54	3.61	1.03
	Minimum	0.08	0.20	1.65	1.43	1.52	0.44
Nitrite NO_2	Mean	0.001	0.001	0.006	0.002	0.001	0.002
	Maximum	0.001	0.001	0.006	0.003	0.001	0.006
	Minimum	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Notes:
1. Not all sample sites were sampled the same number of times. The Kaiser outfall was dry several times.
2. Sample results of less than detectable were not included in the averages.
3. mg/l as N is milligrams per liter as Nitrogen.

Table 12. Little Deep Creek Nitrate and Nitrite Summary

Parameter (mg/l as N)		Little Deep Creek at Colbert Road	Little Deep Creek at Little Spokane Drive
Nitrate NO_3	Mean	0.28	0.49
	Maximum	0.50	0.96
	Minimum	0.11	0.22
Nitrite NO_2	Mean	0.001	0.002
	Maximum	0.001	0.006
	Minimum	<0.001	<0.001

4 MONITORING ACTIVITIES

The USGS currently operates one stream gage in the LSR watershed. The station at Dartford (12431000) has been in operation since 1947 and provides a good long-term record of flow in the watershed except for the Spokane Valley-Rathdrum Prairie aquifer contribution in the lower reaches. The SCCD also operates five stream flow stations within WRIA 55.

The Pend Oreille Conservation District (POCD) monitored water quality in the Little Spokane River at different sites during the year of 1996-1997 and 1998-1999. At present, however, the POCD is not involved in any water quality monitoring programs within the LSR watershed.

Ecology is the only entity that is currently involved in water quality monitoring along the Little Spokane River on a continuous basis. Table 13 contains the names and approximate locations of the fourteen historic sites that have been periodically sampled. The locations of these sites are shown on Figure 14. It should be noted, however, that not all of the sites have been monitored for the same period of time. In fact, as illustrated in Table 13, consistent sampling has only been conducted at one location (55B070). Seven of the fourteen locations were only sampled for a single season.

Table 13. stations in the Little Spokane Watershed

Map ID	Station Code	Station Name	Class	Last Year Sampled	Sampling History				
					1960's	1970's	1980's	1990's	2000's
1	55B070	Little Spokane R near Mouth	A	2004		x x xxx	xxxxxxxxx	xx xxxxxx	xxxxx
2	55B075	Little Spokane @ Painted Rocks	A	1999				x	
3	55B080	Little Spokane R near Griffith Spring	A	1991				xx	
4	55B082	Little Spokane R above Dartford Creek	A	1999				xx x	
5	55B085	Little Spokane near Dartford	A	1966	xxxxxxx				
6	55B090	Little Spokane R above Wandermere	A	1973		x			
7	55B100	Little Spokane R above Deadman Creek	A	1994				xx x	
8	55B200	Little Spokane @ Chattaroy	A	1999				x x	
9	55B300	Little Spokane River @ Scotia	A	2004					x
10	55C065	Deadman Cr nr Mouth	A	1994				x	
11	55C070	Peone (Deadman) Creek above L Deep Cr	A	2004				xx	x
12	55C200	Deadman Cr @Holcomb Rd	A	2004					x
13	55D070	Deer Cr near Chattaroy	A	1994				x	
14	55E070	Dragoon Cr near Chattaroy	A	1994				x	

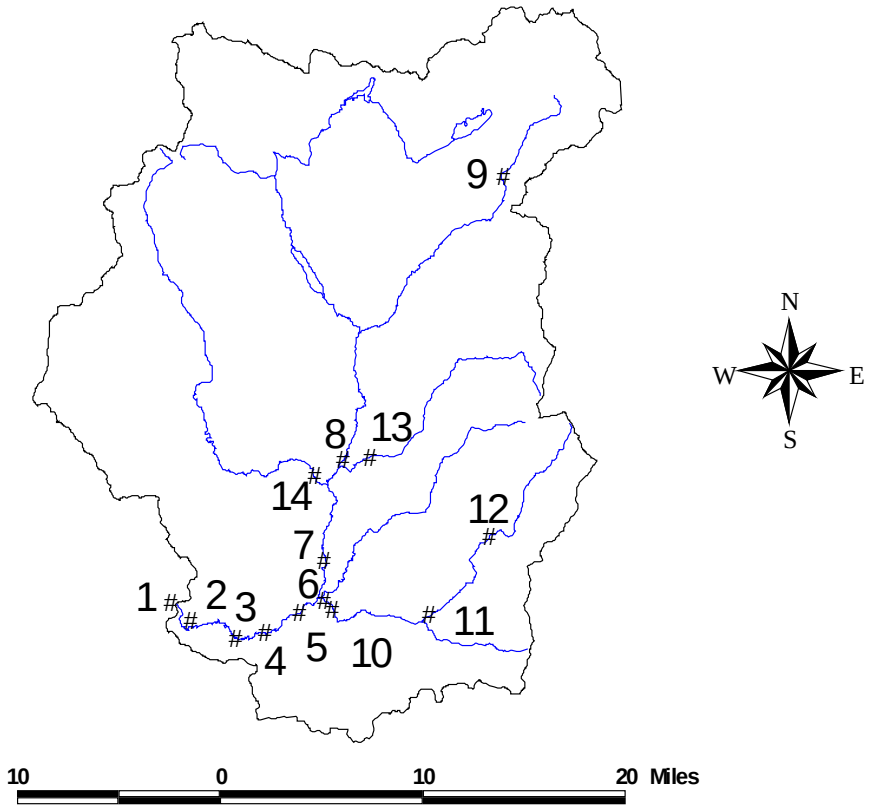


Figure 14. Water quality data monitoring sites in the Little Spokane watershed operated by Washington Department of Ecology

5 HISTORICAL SURFACE WATER QUALITY DATA ASSESSMENT

Ecology has monitored water quality at fourteen different sites for fourteen parameters along the Little Spokane River and its tributaries. However, as was indicated in Table 13, many of the monitoring locations were only sampled for one or two intermittent years. The remainder of this chapter interprets data from these sites to determine potential areas of concern and identify where additional data is needed.

5.1 pH

pH measures the hydrogen ion concentration of liquids. Low pH values indicate acidic conditions whereas high values represent alkaline conditions. In other words, the lower the pH is, the more hydrogen (H^+) ions there are in the water. Neutral values of pH are around 7 on a log-scale. The State of Washington criteria for pH ranges from 6.5 to 8.5. pH can be affected by the photosynthesis process during which algae and aquatic plants consume dissolved carbon dioxide present in the form of carbonic acid. Shifting the chemical equilibrium of the carbonate buffering system liberates hydroxyl ions as indicated by an increasing pH (Butkus, 2002). As a result, most pH problems in the State of Washington are associated with high (basic) pH conditions that are tied directly to point and nonpoint sources of nutrients and the eutrophication process.

Violations of the pH criteria have occurred in Deadman Creek above Little Deep Creek (Ecology station 55C070) in 1990 and 1991 with pH values ranging from 8.6 to 9.4. Furthermore, in 1994, on Deadman Creek near the mouth (Ecology station 55C065), the pH once again exceeded the criteria as it rose to 8.6. It is not clear whether or not other violations have occurred on Deadman Creek since that time due to lack of consistent data collection at these stations. Except for the station at the Little Spokane near mouth (55B070), the remaining Ecology water sampling stations in the watershed did not indicate any violations of the pH criteria for any of the sampled years. Even at station 55B070, pH violations have only occurred rarely. A pH value of 8.6 occurred twice in 1978, once in 1979 and again in 1996, but such violations have not been seen in the other years. The data showed that the pH values were generally not less than 7 at any of the sites. The exceptions occurred at station 55B070 in October of 1977 and, as shown in Figure Figure 15, again in May and June of 2000. None of these values were below the 6.5 pH criteria.

While water quality criteria have not been violated, Figure 15 does indicate that many of the pH values in recent years have been greater than 8. When compared to the values collected in the 1970s and 1980s, there does appear to be a discernable increasing trend. In the years prior to 1991, the average value of the 208 pH samples taken was 7.91. Since 1993, the average value of the 125 pH samples taken has been 8.01; a small increase of 0.1 units. These increases are not temporally distributed. Figure 16 illustrates the average fluctuation of pH during the year. Peak values occur in July, August, and September coinciding with peak eutrophication and algae growth cycles. However, due to the fact that photosynthesis activities stop without sunlight, pH measurement in evening hours is required to support this suggestion.

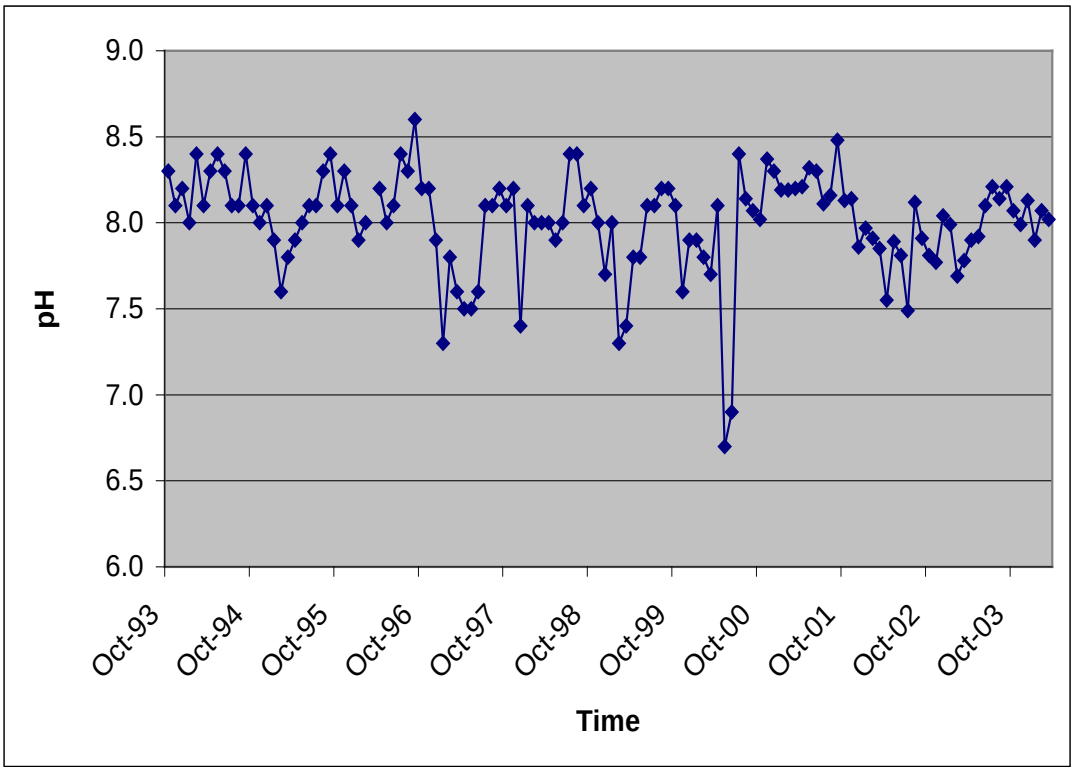


Figure 15. Recent pH values for Station 55B070 near mouth of LSR

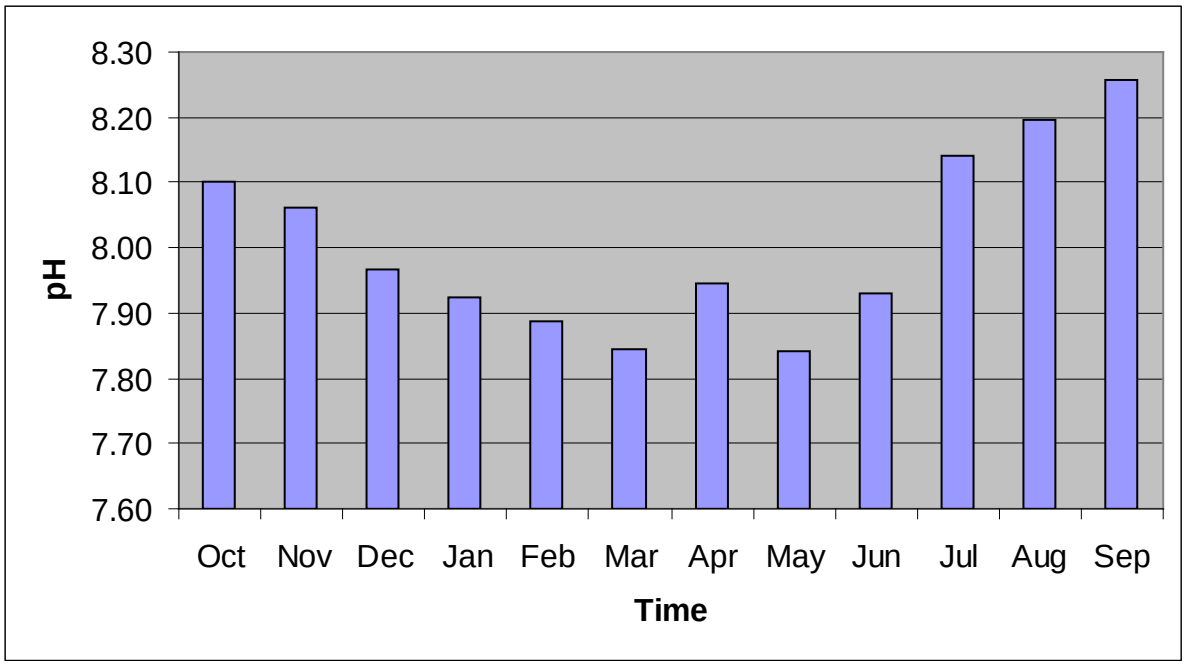


Figure 16. Average pH values at 55B070 from October 1993 through March 2004

It should be noted that mathematically pH results cannot be averaged, because the formal definition of pH is the negative logarithm of the hydrogen ion activity. However, in practice, we always average pH results due to the fact that: (1) If we believe pH is a indicator for acidity and alkalinity, the average value can give us "average" condition; (2) The concentration is usually very small (for example, pH=7 means [H+]=0.0000001). The pH for stream flow is usually between 6-8, i.e. [H+]=0.000001-0.00000001. The average value of pH is nearly equal to transformed-average value.

In addition to the Ecology samples, the Pend Oreille Conservation District (POCD) conducted a water quality monitoring program from October 1998 to September 1999 at ten sites on the LSR that also measured pH. The locations of these sites are shown in Figure 17. The results are presented in Appendix B. Out of the ten sites that the POCD monitored, six new sites were chosen by the POCD and four sites were existing Department of Ecology monitoring sites. Site 1 was three miles downstream from the headwaters of the Little Spokane River (LS1). Site 2 was located in Elk Park on Camden Road (LS2). Site 3 was located on the West Branch of the LSR at the outlet of Eloika Lake off of the Eloika Lake Road (LS3). Site 4 was located downstream of the West Branch confluence as the river goes under Milan Road (LS4). Site 5 was at the downstream of the confluence of the Dragoon Creek (LS5) and Site 6 was located downstream of the confluence of Deep and Deadman Creeks (LS6). The remaining four ecology monitoring sites were at stations:

55B200 Little Spokane River at Chattaroy
55B082 Little Spokane River at Dartford Creek
55B075 Little Spokane River at Painted Rocks
55B070 Little Spokane River near mouth

The pH values the POCD recorded were greater than 8.5 for sites LS2, LS3, LS5 and LS6. The pH values for all other sites were between 6.5 and 8.5. The violation occurred during the months of March for LS2 and LS5, April for LS2, LS3, and LS6 and July for LS3. It was reported that the high pH seen at LS3 was due to the over heating of the pH meter. So the pH was suspected to be less than 9.

Water quality assessments of Deadman and Little Deep Creek (Appendix C) done by the SCCD during the years 2001-2002 showed that the pH ranged from 6.82- 7.80 and for the Little Deep Creek the pH ranged from 6.57 and 7.76. It was seen that the pH for both creeks was lower in the upstream than in the downstream sections, which could possible be due to addition of nutrients and eutrophication processes in the downstream reaches. Similar pH characteristics were seen in the study carried out in the Dragoon Creek basin. The pH was less than 8 almost all of the time. None of the sites violated the pH standard (Lundgren, 1998).

There is little variation in pH values along the entire LSR mainstem as the pH values generally fluctuate between 7 and 8. Looking at the pH trends, it is observed that the values are not consistent throughout the day. The pH values are higher during the afternoon (from 12 to 4 p.m.) than during morning or evening hours. Figure 16 also demonstrated that pH values tend to be greater during summer periods (July-September) which also confirms that photosynthetic processes are be contributing to pH values. Under normal growth conditions, photosynthesis by

algae or other aquatic plants uses water and carbon dioxide to produce carbohydrates (sugar) and oxygen according to:

$$6\ H_2O + 6\ CO_2 \leftrightarrow C_6H_{12}O_6 + 6\ O_2$$

However, when the rate of photosynthesis exceeds the rate of CO_2 diffusion into the water column, plants can also use carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-), or carbonate ions (CO_3^{2-}). These equations can be expressed as:

$$6\ H_2CO_3 \leftrightarrow C_6H_{12}O_6 + 6\ O_2$$

$$4\ H_2O + 6\ HCO_3^- \leftrightarrow C_6H_{12}O_6 + 7\ O_2 + 2\ OH^-$$

$$14\ H_2O + 12\ CO_3^{2-} \leftrightarrow 2\ C_6H_{12}O_6 + 17\ O_2 + 4\ OH^-$$

The last two equations produce free hydroxyl ions (OH^-) which raises the pH during photosynthesis. During evening and pre-dawn conditions, respiration exceeds photosynthesis and the process essentially reverses itself and the pH decreases.

Overall, pH does not seem to be a significant problem in the LSR as most pH values have been within the range of State criteria. However, pH may become a problem if additional nutrients are added to the river as a result of future growth. pH trends examined near the mouth of the LSR do seem to indicate values are slowly increasing.

Although pH values are currently not a large concern, monthly monitoring, as well as targeted continuous sampling, should be conducted to help understand the complex interactions between nutrients, dissolved oxygen and pH.

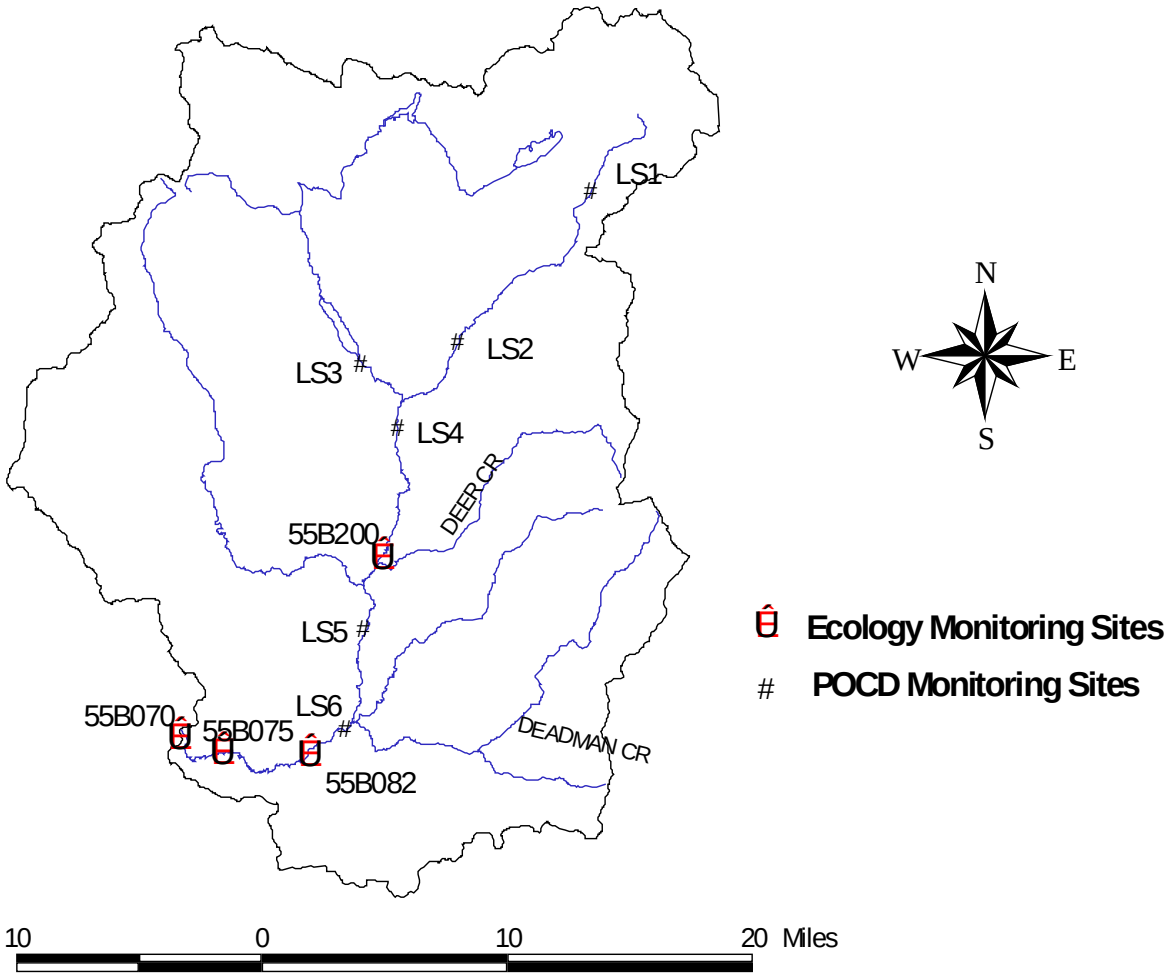


Figure 17. POCD Monitoring sites for the Little Spokane Watershed

5.2 Temperature

Temperature affects the physical, biological and chemical characteristics of a stream. It influences the amount of dissolved oxygen present in a stream, the rate of photosynthesis by algae, the metabolic rates of aquatic organism and the sensitivity of organism to toxic waste, parasites and diseases. Water quality standards set by the State of Washington requires water temperatures to be less than or equal to 18^{o}C.

Water temperatures measured at a number of stations in the Little Spokane River Basin have violated the state's temperature standard. Dragoon Creek near Chattaroy (55E070) reported a stream temperature of 21^{o}C in the month of August, 1994. Data from Peone Creek above Little Deep Creek (55C070) indicated a number of violations during the year 1990. It showed temperatures of 20.6^{o}C, 20.7^{o}C, and 17.9^{o} C during the months of July, August, and September, respectively. Deadman Creek near the mouth (55C065) reached a temperature of 18.4^{o}C during the month of August that same year. The station at Chattaroy (55B200) showed temperature violations of 18.1^{o}C in 1994 and 19.3^{o}C and 18.4^{o}C in 1999. The Little Spokane River above Deadman Creek (55B100) station recorded temperatures of 21.8 ^{o}C and 21.6^{o}C during the months of July and August, 1990. In1973, the station at Wandernere (55B090) had temperatures of 19.6^{o}C and 18.6^{o}C. The temperature standard has been violated many times during the months of August and September at he Little Spokane River near Dartford (55B085) station. The water temperatures ranged between 18-23^{o}C in the years of 1960, 1961, 1962, 1963 and 1965. As illustrated in Figure 18, it is interesting that temperature violations at the mouth of the Little Spokane River (55B070) did not occur even once during the sampling period. Similar results are shown with the continuous temperature data as illustrated by the 2002 water year example in Figure 19. It is hypothesized that the cooling effects of the large volumes of groundwater seepage from the Spokane Valley/Rathdrum Prairie aquifer into the lower sections of the river helped mitigate upstream warming trends.

In the study carried out by POCD, continuous temperature monitoring was done for sites LS1, LS3, LS4 and LS6. Out of these sites, only the temperatures on the west branch at LS3 were consistently above the required criteria. It also had the highest temperature of 28°C. Warm water released downstream from the productive Lake Eloika seemed to be at least partially responsible for the high temperatures. Temperatures did not exceed the State's criteria for sites 55B082, 55B075, and 55B070. For sites LS2, 55B200, and LS5, the stream temperatures ranged between 19 and 24°C during months of July and August. The highest temperatures for all the sites were in the months of July and August. The lowest temperature of 0.9°C was seen for sites 55B200 and 55B082 in the month of February.

Monitoring performed by the SCCD at several different sites in the Dragoon Creek watershed between the years of 1994-1996 showed four violations of the stream temperature standard. Three of the exceedences occurred along the mainstem of Dragoon Creek with temperatures ranging from 19.0 to 22.5^{o}C. The remaining exceedence occurred along the west branch tributary and was measured 19.3^{o}C (Lundgren, 1998). Deadman and Little Deep Creeks did not show any temperature violations during the study (SCCD, 2003). The temperature in Deadman Creek was higher than in the Little Deep Creek, probably because it has been impacted more due to urbanization downstream. However, none of the measurements were above 18^{o}C.

The historic data demonstrated that temperatures are high throughout much of the watershed in the months of August and September. Most of the temperature violations have occurred during the months from June to August. Lack of shade/vegetation, low instream flows, and reduced groundwater impacts, could have contributed to the high temperatures. Also, excess amounts of sediment erosion could have helped lead to higher temperatures. Streambank erosion and sediment deposition increase channel widths and decrease water depths thereby contributing to increased water temperatures. The limited amount of available data suggests that high temperatures in some stream sections have been historical problems.

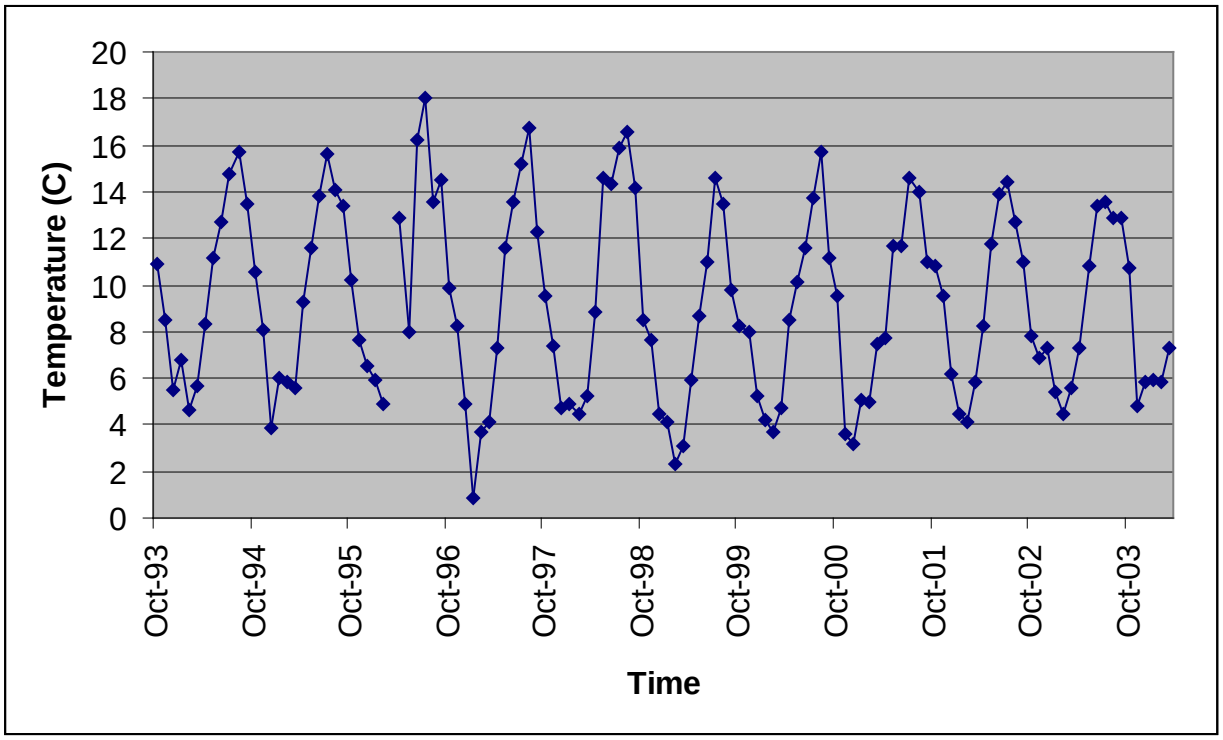


Figure 18. Recent grab sample temperatures at 55B070

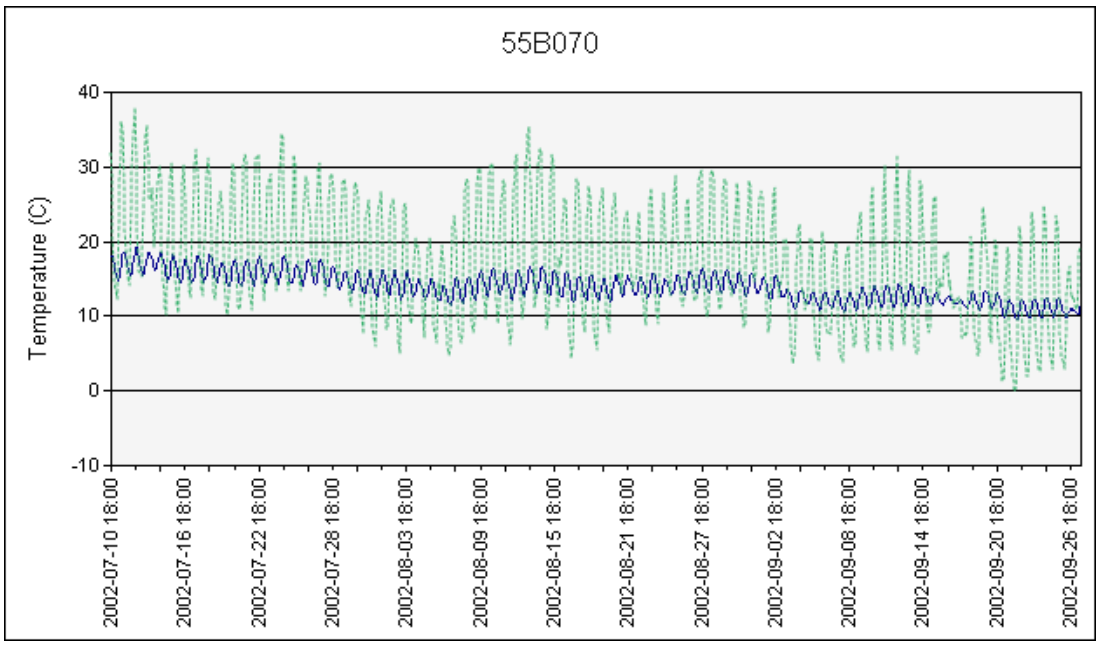


Figure 19. Continuous air/water temperature data from Water Year 2002

5.3 Dissolved Oxygen

Dissolved oxygen is essential for the survival of aquatic species. Oxygen affects growth and development and determines whether an aquatic organism will survive. The Washington state criteria for dissolved oxygen require daily minimum DO concentrations to be greater than 8.0 mg/L for the types of streams in the LSR drainage basin. Dissolved oxygen concentrations have generally been above the state criteria at the monitoring sites maintained by Ecology, except at the mouth of the Little Spokane River. Historically, in the monitoring period from 1971-1991, violation of dissolved oxygen at station 55B070 occurred only three times; once in 1977 with a dissolved oxygen concentration of 7.8 mg/L and twice in 1987 with reported values of 7.7 and 7.8 mg/L. From 1993 onwards, dissolved oxygen violations have occurred more frequently. In 1997, violations occurred three times with dissolved oxygen ranging from 7.0 to 7.9 mg/L. In 1998 and 1999, dissolved oxygen concentrations of 7.4 and 7.3 mg/L were seen, respectively. In 2000, one violation of 7.97 mg/L had occurred. From this scenario, it can be indicated that the dissolved oxygen has been decreasing at this station compared to the past record. One possible reason could be the increased urbanization near the downstream end of the Little Spokane River. Another reason for concern is that these daytime values do not represent minimum DO concentrations that generally occur just before dawn. Consequently, continuous DO monitoring is necessary during critical summer periods.

In spite of these violations, the average monthly concentrations remain quite good. Figure 20 presents the average monthly DO concentrations over the past 11 years. Seasonally, the lowest DO values occur in May and then increase slightly through the summer months. The May low in DO is prior to the major photosynthetic production and since the data have been collected during the day, some variation during evening hours might be expected. Still, these results are

somewhat surprising since DO saturation is inversely related to temperature. At standard pressure and zero salinity, the relationship for DO saturation (DO_{sat}) can be expressed as (Thomann and Mueller 1987):

$$Ln\left(DO_{sat}\right) = -139.34411 + \frac{1.575701x10^{5}}{T+273.15} - \frac{6.642308x10^{7}}{(T+273.15)^{2}} + \frac{1.2438x10^{10}}{(T+273.15)^{3}} - \frac{8.621949x10^{11}}{(T+273.15)^{4}}$$

where T is in $^{\circ}$C, DO is in mg/L, and Ln stands for natural logarithm. Pressure and salinity corrections can be easily applied to this expression.

DO concentrations on several tributaries have identified minimum DO violations more severe than the Ecology sites on the mainstem LSR. In monitoring work carried out on Dragoon Creek during the years of 1994-1996, only 26 of 171 samples met the state dissolved oxygen criteria of 8 mg/L (Lundgren, 1998). Out of the nine sites sampled, six sites violated the state standard. During the study carried by the SCCD, Deadman Creek had dissolved oxygen concentrations as low as 3.39 mg/L. And, while Little Deep Creek usually met the standard, a dissolved oxygen concentration of 7.45 mg/L was reported for one of the downstream sample locations. In the 1999 study carried out by POCD, site L3 violated the DO standard.

From the historical data it is observed that DO is of concern in Deadman and Dragoon Creeks and, to a lesser extent, the lower reach of the LSR. Trends indicate that the DO concentrations are higher during morning hours which is not typical of photosynthetic oxygen production unless travel times impact timing. This trend is reverse to that of the temperature trend. It can also be concluded that dissolved oxygen decreases in the downstream direction (see Figure 21). This could be due to the lack of tall vegetation downstream and increased air temperatures. It is seen that the sites that have violated the criteria had higher temperatures compared to the sites that had lower temperatures. There is an inverse relationship between temperature and dissolved oxygen. Sites that have low temperatures have high dissolved oxygen concentrations and vice versa. This suggests that high temperatures may be the main cause for DO standard violations.

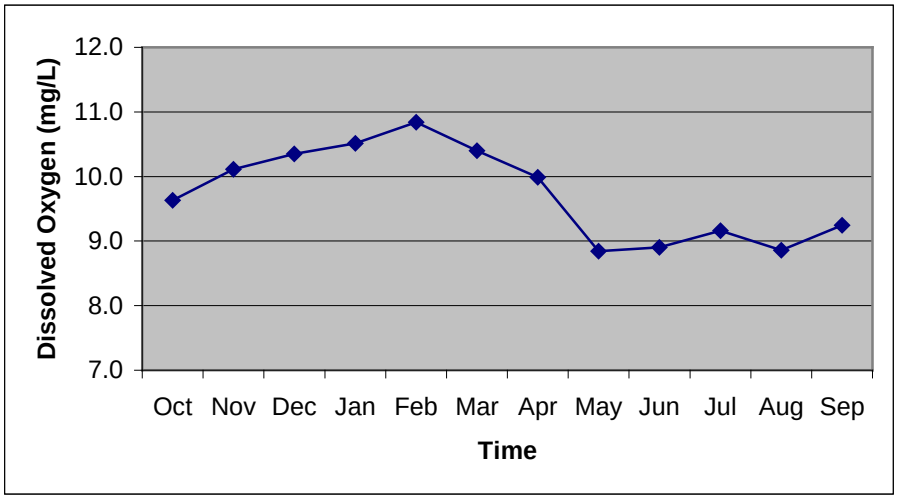


Figure 20. Average monthly Dissolved Oxygen at 55B070 site near mouth of LSR

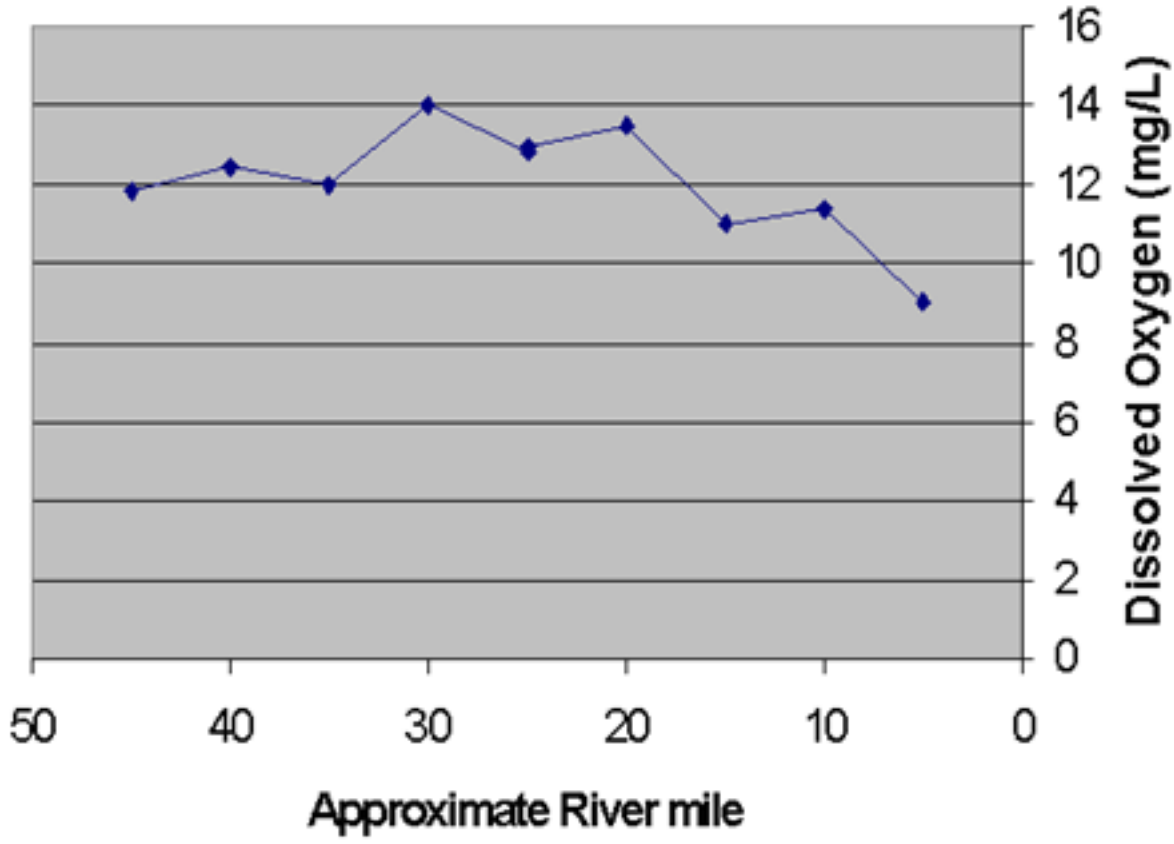


Figure 21. DO trends along the mainstem of the LSR (Golder, 2003)

5.4 Fecal Coliform

Fecal coliform data indicate the quality of water in terms of the presence of human or animal feces. Fecal coliform bacteria generally do not pose a direct danger to people or animals but they indicate the potential presence of other disease-causing bacteria, such as those that cause typhoid, dysentery, hepatitis A, and cholera. The State of Washington Class A freshwater criteria for fecal coliform requires that the geometric mean value for fecal coliform colonies(c) not exceed 100 colonies/100 mL of water and not more than 10 percent of all samples collected and used for calculating the geometric mean value can exceed 200 colonies/100 mL (Ecology 1997).

Violations of the fecal coliform standard have been seen at several of the stations monitored by Ecology in the LSR basin. Violation has occurred at the Deadman Creek near mouth station (55C065) with coliform counts of 330 c/100 ml and 500 c/l00 ml. The Little Spokane River at Deadman Creek station (55B100) has had fecal coliform counts as high as 230c/100 ml. At the mouth of the Little Spokane River, violations occurred in 1982 with coliform count of 280 c/100 ml and in1986 with 320 c/100 ml in the month of January. A record high of 520 c/100 ml was seen in 1991, but such violations were not seen in the preceding and succeeding years. In a study conducted on Dragoon Creek, sites at Oregon and Crawford roads on the mainstem of Dragoon

exceeded the criteria of geometric mean of 100 c/100 ml with recorded values of 116.2 and 142.6 c/100 ml, respectively. Furthermore, Beaver Creek and Huston Creek exceeded the criteria with geometric means of 117.9 and 142.6 c/100 ml. Figure 22 exemplifies the data collected at the long-term Ecology station 55B070 for the most recent period of record. Although recent violations have occurred in August, a review of the entire period of record shows violations also occurred in other months as well. Figure 23 illustrates this point. Data collected in 1999 at several stations along the mainstem of the LSR demonstrate temporal variations although some general spatial correlations can be observed. High values were seen in both winter and summer months. Some dilution, due to the spring freshet, was observed in March. Overall, the data and violations did not illustrate or occur in any consistent manner.

As seen from the above data assessment, fecal coliform is of concern in Deadman and Dragoon Creeks as well as the Little Spokane River. One of the major sources of coliform is the agricultural setting that is dominant in the river basin. Septic systems in suburban/rural housing can also be a major contributor of fecal coliform. Urban and suburban stormwater are other sources of fecal coliform generally due to pets.

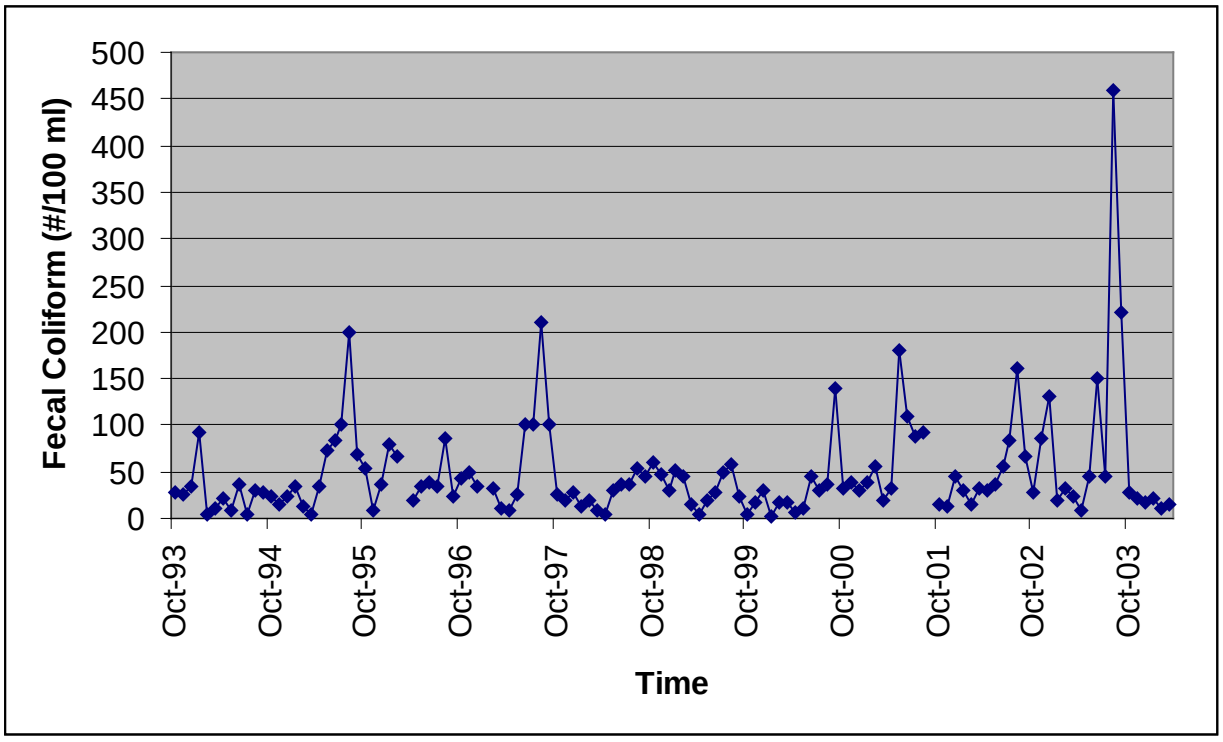


Figure 22. Recent data for fecal coliform at 55B070

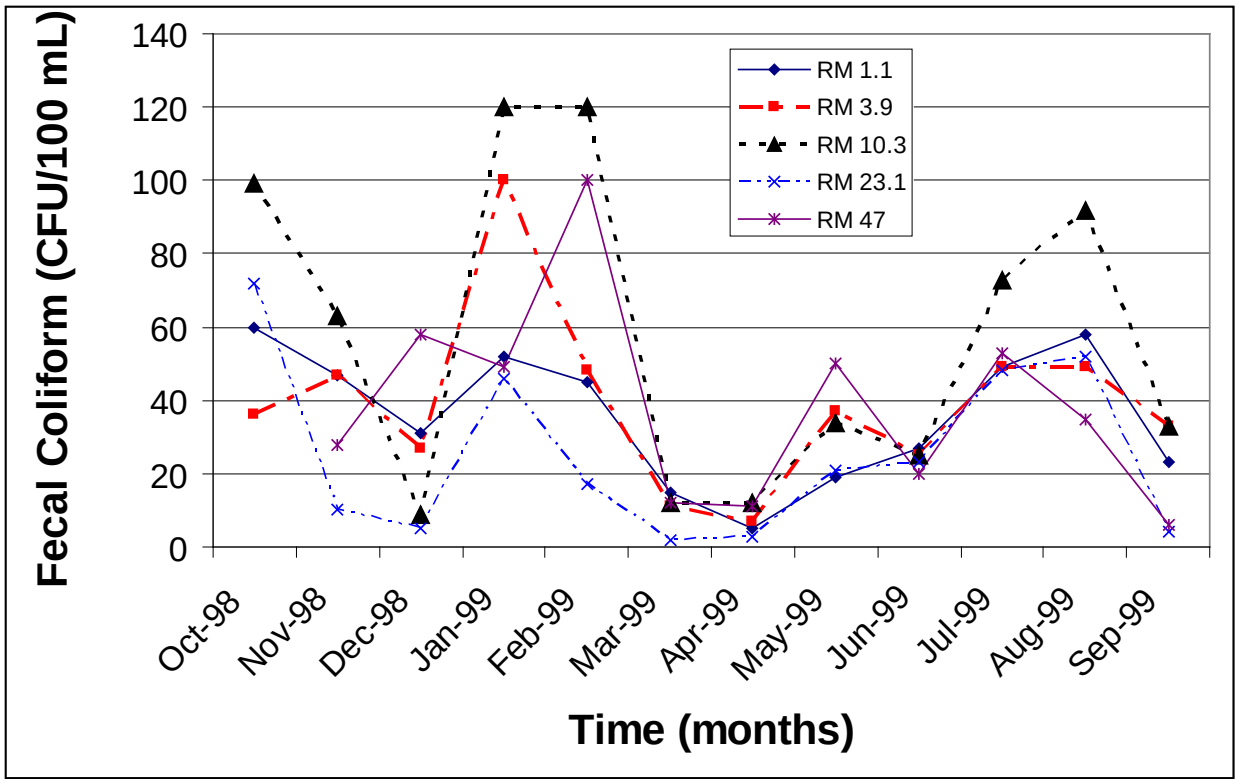


Figure 23. Spatial and temporal variations in Fecal Coliform counts

5.5 Nitrogen

Nitrogen is an essential element for plant growth as well as a common element in air. However, excess amount of nitrogen in available forms can result in water pollution in terms of excess plant/algae growth (eutrophication) particularly if the waterbodies are not limited by available phosphorus concentrations. Among the potential adverse effects of nutrient enrichment are algal blooms, increased incidence of toxic algal blooms, dissolved oxygen fluctuations, taste and odor problems, and altered algal community composition. Nitrogen exists in nitrate, nitrite, ammonia and organic nitrogen forms. All of the nitrogen forms are biologically interchangeable and are components of the nitrogen cycle; however nitrate and ammonia are generally the species of concern. Nitrate poses a health concern if it is reduced to nitrite, however such reducing conditions are unlikely in surface waters. There is no specific Washington State surface water quality standard for nitrate at this time. The US EPA recommends a limit for drinking water supply that is 10 mg/L for nitrate but these values are seldom exceeded in surface water supplies.

The nitrate/nitrite levels have been less than 0.5 mg/L at all the Ecology water quality stations in operation. The levels were greater during winter time periods, especially during October, November, December and January. For Deadman and Little Deep Creek, the nitrate values were lower in the upper reaches but were higher below the springs in both creeks (SCCD, 2003). For Deadman Creek the nitrate values increased from 0.01 mg/L upstream of the spring to 1.01 mg/L near the mouth. The spring had nitrate values ranging from 1.80 to 7.86 mg/L. Similar results

were seen in the case study carried out by POCD. Nitrate and nitrite concentrations seemed to increase slightly as the flow moved downstream. This is because land use along downstream reaches of the river is predominantly urban/rural housing with septic systems, with some agricultural sources also contributing.

The term "ammonia" refers to two chemical species that are in equilibrium in water (NH_3, un-ionized and NH_4^+, ionized). In addition to promoting algae growth, ammonia can be toxic to aquatic species including fish. Ammonia toxicity is generally attributed to the un-ionized form (NH_3), as opposed to the ionized form (NH_4^+). The partitioning between the un-ionized and ionized forms of ammonia is extremely sensitive to pH and moderately sensitive to temperature. As the pH increases, less H^+ ions are available so the fraction of NH_3 increases significantly. For example, at 20°C (68°F), the fraction of total ammonia in the un-ionized phase is only 0.00396 at a pH of 7 compared to 0.284 at a pH of 9. Ammonia concentrations were less than 1 mg/L for all the Ecology stations, except for station 55B070 where a peak ammonia concentration of 1.4 mg/L was recorded in 1981. However, even at this station, since 1993 no ammonia concentrations greater than 0.1 mg/L have been reported. At the six sites operated by POCD, the ammonia concentrations remained below 1.5 mg/L. There was little difference in concentration between upstream and downstream sites. At these reported ammonia levels, toxicity to fish is insignificant.

There is a current effort by the US EPA to implement a national strategy for developing nutrient information and working with states and tribes to adopt nutrient criteria as part of State water quality standards. These criteria will initially be targeted at total nitrogen and total phosphorus. Total nitrogen in water is comprised of dissolved inorganic (nitrate and ammonia) and organic nitrogen and particulate organic and inorganic nitrogen, minus N_2 gas. Using the aggregation of Level III ecoregions shown in Figure 24, US EPA created 14 regions for the entire country and then proposed nutrient criteria for these regions. The Little Spokane River falls within region II, the Western Forested Mountains. The criteria setting process and water quality standards regulations allow states to:

1) develop their own criteria which reflect more locally representative conditions;
2) use different techniques to develop criteria as long as they are protective of designated uses and scientifically defensible; and
3) conduct use attainability studies and refine their use designations.

The US EPA recognizes these regions are rather coarse and therefore is encouraging states and authorized tribes to refine the published criteria to better reflect local conditions. Specific procedures for refining the criteria are presented in EPA's Technical Guidance Manuals. Additional data and analysis that states and authorized tribes can bring to the process of nutrient criteria development include refined physical classification, reference site data, quantified relationships between nutrient levels and biological effects, nutrient loading analyses, and hydrologic and aquatic life effects modeling.

Table 14 presents the proposed nutrient criteria for Region II. The total nitrogen criteria proposed by the US EPA is well below the nitrogen concentrations measured for this watershed. The average total nitrogen concentration reported at Ecology's long-term 55B070 station since 1993 is 1.21 mg/L.

Figure 24. Aggregation of Level III Ecoregions for nutrient criteria

Table 14. Proposed nutrient criteria for streams and lakes (US EPA, 2002)

Ecoregion	Streams and Rivers			
	Total Nitrogen (mg/L)	Total Phosphorus (µg/L)	Chlorophyll *a* (µg/L)	Turbidity (FTU/NTU)
II	0.12	10.00	1.08	1.30 N
Ecoregion	Lakes and Reservoirs			
	Total Nitrogen (mg/L)	Total Phosphorus (µg/L)	Chlorophyll *a* (µg/L)	Secchi (m)
II	0.10	8.75	1.90	4.50

While the State of Washington has not currently endorsed these values, the latest proposed revisions to the WAC do contain numeric limits for phosphorus in lakes for several ecoregions.

5.6 Phosphorus

Like nitrogen, phosphorus is also essential for plant growth and excess amounts can also lead to eutrophication. No Washington State surface water criterion has been established for phosphorus although historically US EPA recommended 100 ug/L as the upper limit of total phosphorus. Concentrations in excess of this recommended value occurred four times during the study carried out by POCD. Site LS5 reported a value of 112 ug/L, Site LS6 had a concentration of 127 ug/L, and Site 55B082 had a value of 106 ug/L during February. Site LS5 also had a concentration of 103 ug/L in March. The concentrations increased from upstream to downstream as seen in Figure 25, possibly due to the result of urbanization and agricultural practices downstream of the river. As shown in Table 14, under the new guideline, the recommended value for the LSR would be reduced to 10 ug/L. This would likely create significantly more violations.

Unlike nitrogen, phosphorus is a concern in the tributaries of the LSR such as in Dragoon Creek, Deadman Creek, and Little Deep Creek. The trend illustrates that phosphorus concentrations are higher in the winter months from January to April likely as a result of runoff carrying the nutrient to the stream. While these months do not represent the most critical periods in terms of algae growth, the role of phosphorus cycling may make the nutrient available in later months. Phosphorus concentration peaks in January through April are significant for the Spokane River and Long Lake DO TMDLs (Cusimano, 2004).

Based on the information available, phosphorus concentrations should be measured as part of the TMDL study. Although nitrogen is not a primary concern, the interaction between N and P will require that nitrate and ammonia are also sampled.

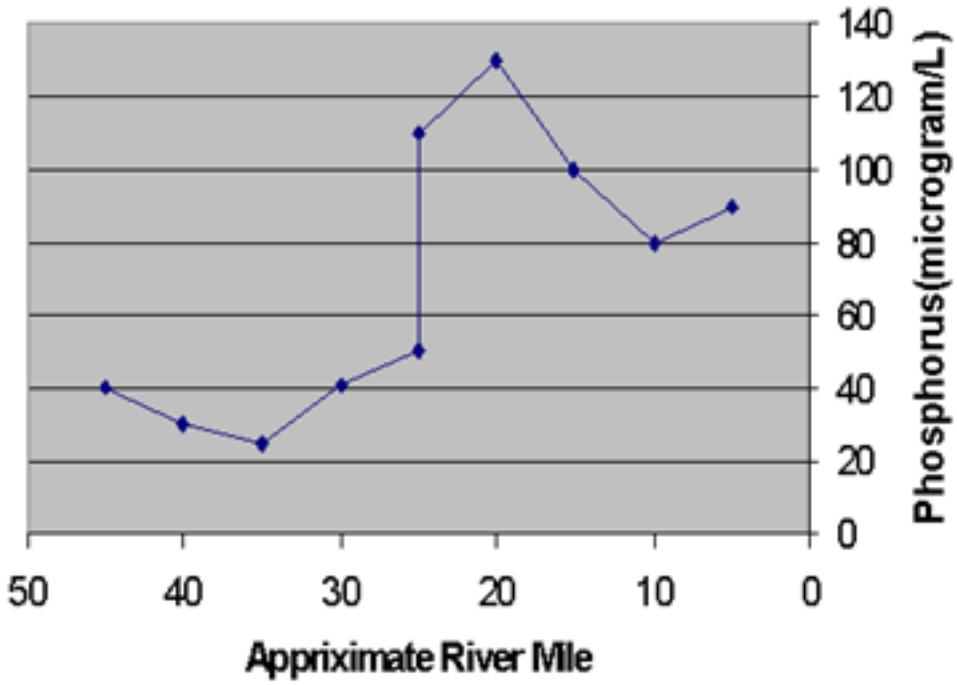


Figure 25. Phosphorus trends in the Little Spokane River

Nutrient conditions alone are not sufficient to identify potential problems. Algae growth during summer months may reduce the concentrations on nitrogen and phosphorus. Fluctuations in dissolved oxygen concentrations during these periods are used to further identify potential eutrophication problems.

5.7 Turbidity

Turbidity is an optical property that causes light to be scattered and absorbed rather than transmitted in straight lines. Suspended matter such as clay, silt, finely divided organic and inorganic matter, plankton and other microscopic organism in water cause turbidity concentrations to increase. The State of Washington water quality standards requires that turbidity not exceed 5 NTU over the background turbidity when the background turbidity is 50 NTU or less, or have more than a 10 percent increase in turbidity when the background turbidity is more than 50 NTU.

In general, turbidity levels are greater during winter periods than in summer months. This is probably because winter snow and rainfall in the watershed cause additional surface water runoff that transports more sediment and other small particles into the stream. In addition, there is less vegetative cover to reduce erosion rates. In a POCD study, Figure 26 demonstrates that turbidity increases from upstream to downstream. In most cases, turbidity increased from Site LS6 onwards and reached a maximum at the mouth of the Little Spokane River. This is because a number of tributaries such as Deadman Creek, Dragoon Creek, and Little Deep Creek are

contributing their sediments to the mainstem of the LSR. Another reason could be due to the difference of vegetation between upstream and downstream of the river. Vegetation dominates the upstream of the river, so sediments are trapped by the vegetation. However as there is less vegetation in downstream, there is no sediment trapping source and as a result, most of the sediments ends up in the river.

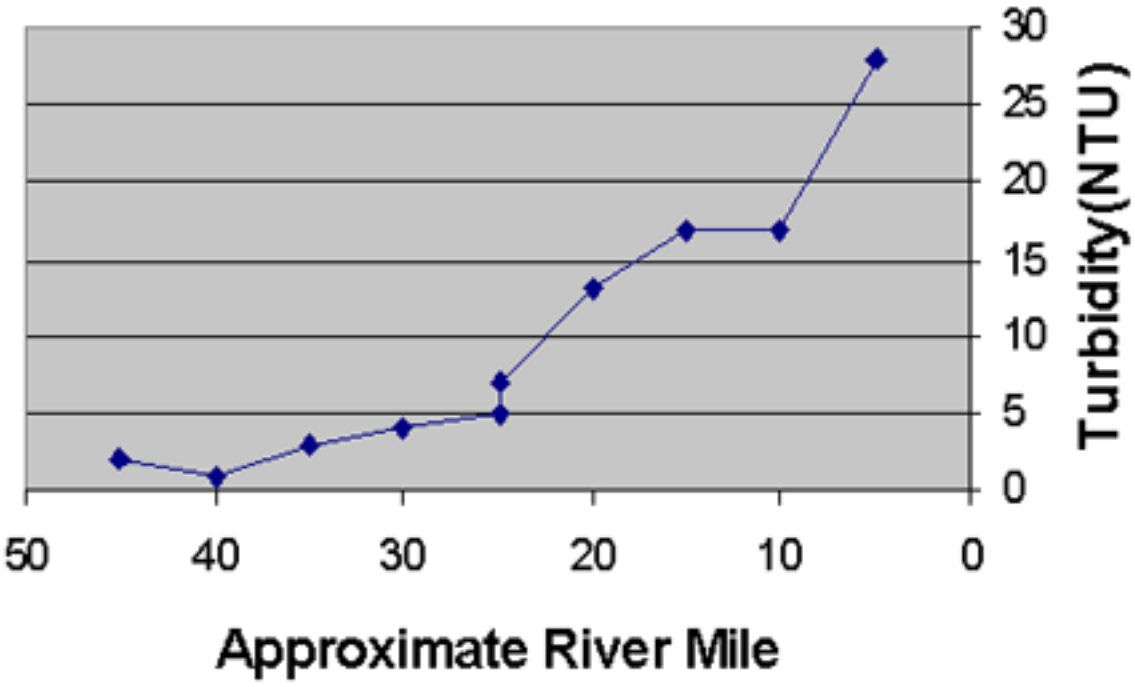


Figure 26. Turbidity trends in the Little Spokane River

The data in Figure 26 represent a snap-shot in time rather than monthly sampling results. As indicated by the turbidity parameter on the 303(d) list, turbidity concentrations in some months exceed the State's standard.

5.8 Suspended Sediment

Suspended sediments are particles that are transported in the water column. There is often a direct relationship between turbidity and suspended sediment. At stations where turbidity is high, suspended sediment is also high. The erosion and runoff mechanisms that contribute to turbidity also impact sediment. As a result, suspended sediment concentrations are higher during winter periods than in summer time.

While Washington State does not have a specific standard for suspended sediments, many pollutants (e.g., phosphorus) are associated with sediment. Furthermore, deposition of sediments may cause flooding or be detrimental to aquatic organisms. High suspended sediment

concentrations may also indicate excessive streambank scour due to hydrograph modifications in urbanizing areas or poor agricultural practices.

Because turbidity is easier to measure, a correlation between turbidity and suspended sediment should be developed if possible. This will require TSS (total suspended solids) samples be collected in conjunction with turbidity measurements until such time as the relationship can be developed.

5.9 Metals

Ecology had sampled ten different heavy metals between 2001 and 2002. No definite patterns of increase or decrease in metal concentrations were seen during the sampling period. Furthermore, the concentrations did not exceed water quality standards. Aluminum levels in Deadman and Dragoon Creeks are reported as a Category 2 pollutant in the 303(d) listing. Overall, however, metals are not a major concern in the Little Spokane Watershed.

5.10 PCBs

Polychlorinated biphenyls (PCBs) are a potential concern in the LSR because of a preliminary study conducted by Ecology (1995). This study found PCB concentrations in the tissue of largescale suckers (catostomus macrocheilus) of 440 µg/Kg. This study sampled fish in the reach ranging from RM 1 to RM 8 on the mainstem of the river. Since fish are somewhat migratory, the study did not conclude that the PCBs came from the LSR watershed. Similar concentrations were found in the Spokane River. A separate study on PCBs is currently underway at Ecology so they will not be considered in this QAPP.

6 DATA GAP ANALYSIS

As was presented in the previous chapters, water quality sampling has occurred somewhat sporadically in the Little Spokane River basin since 1960 (Ecology 2000). Over the years, Ecology has collected samples at 14 different water quality stations within the watershed. This is misleading because only one or two stations were operated in any given year. In fact, the maximum number of stations ever operated by Ecology in a single year was six, with three of those being on the mainstem LSR. Even for the few stations that have been monitored frequently, there is often a wide gap between the sampling years. As a result, no comprehensive sampling plan has ever been implemented in the basin.

Because Ecology sampling location 55B070 is the only long-term site routinely monitored over the past decade, it is difficult to quantify trends for any location other than near the mouth of the Little Spokane. The quality of the upstream tributaries can significantly affect the quality of the downstream river and with the exception of Dragoon and Deadman Creeks, there have been few monitoring stations located on the upstream tributaries of the Little Spokane River. While this is an important reach, the contribution of all the upstream tributaries and the significant ground water inflow makes cause-and-effect analysis impossible.

In examining the water quality data, land use, hydrologic characteristics, and information provided by the local stakeholders, data gaps were identified. This involved interpretation of existing problems at known locations to other stream segments and other tributaries to determine the sampling locations needed to address water quality concerns in the watershed. The following sections present the justification of the proposed locations.

6.1 Stream Segments of Interest

The criteria for monitoring water quality in the Little Spokane River Watershed (WRIA 55) are primarily associated with 1) identifying specific existing or emerging water quality problems and 2) characterizing waters and identifying changes or trends in water quality over time. Included in these monitoring purposes is the need for information to address Ecology's revised 303(d) listing procedure. The emerging and existing categories of concern are the waters currently listed in Category 2 and Category 5. As was previously presented in Table 10, Category 5 listed streams are the most important at the present time but Category 2 listed streams may become important in the future. Also included were the major tributaries where little or no information was available.

Table 15 identifies the tributaries of interest in the LSR basin. These subbasins represent the largest basins in the drainage or streams where the stakeholders identified particular activities that might impair the local surface waters. Known 303(d) listings were also used to select the study watersheds. Table 16 summarizes the known and potential problems for the target watersheds. As indicated, many of the problems in this basin revolve around fecal coliform, temperature, dissolved oxygen, and turbidity.

Table 15. Little Spokane River Basin Stream Segments of Interest

Stream	303(d) status	Land Use
Bear Creek	No	
Dartford Creek	No	
Deadman (Peone) Creek	Yes - 5	Agriculture, Forest, Urban
Deer Creek	No	Forest
Dragoon Creek	Yes - 5	Agriculture, Forest, Urban
Dry Creek	No	
Little Deep Creek	No	Forest, Agriculture
Little Spokane River (upstream)	No	Forest, Agriculture
Little Spokane River (downstream)	Yes - 5	Agriculture, Forest, Urban
Otter Creek	No	
West Branch Little Spokane River	No	Forest, Agriculture

Table 16. Listed Parameters of Immediate and Potential Concern in River Segments

Stream	Category 5 Parameters	Category 2 Parameters
Deadman Creek	Fecal Coliform	Aluminum, pH, Temperature
Dragoon Creek	Fecal Coliform	Dissolved Oxygen, Fecal Coliform, pH, Temperature
Little Spokane River	Total PCB, Turbidity	Dissolved Oxygen, Fecal Coliform, pH, Temperature

Several of the pollutants listed in Table 16 are often associated with excess nutrients. Warm temperatures, combined with excessive nitrogen and phosphorus concentrations, often create conditions where plant and algae growth lead to DO and pH problems. Furthermore, the sources of these nutrients can be from septic systems or nonpoint agricultural runoff that may elevate fecal coliform counts and turbidity/sediment concentrations. These interactions helped guide the selection of parameters discussed in the next section.

The rationale for selecting the proposed monitoring sites varies from watershed to watershed. The following paragraphs explain the reasons for selecting the locations. Table 17 summarizes these explanations. Monitoring near the mouth of the Dry Creek should be done to evaluate if land use practices in that watershed are contributing to pollution in the mainstem of the Little Spokane River. Since no historical record was found on this site, the monitoring of pH, dissolved oxygen, temperature, fecal coliform, and nutrients should be done routinely throughout the whole year. Turbidity and suspended solids should also be measured.

Deer Creek and Dragoon Creek watersheds are also proposed as additional monitoring sites because they represent significant potential sources of flow and contaminants to the Little Spokane River. Nutrients, such as phosphate and nitrate, tend to increase as the river flows downstream. However, it is not clear whether the concentrations of the nutrient are higher in

summer than in winter or vice versa. To assess this pattern we need to monitor nutrients routinely at both the sites. Because of the lack of historical data, Deer Creek should be monitored for the same parameters as other watersheds in the basin. Dragoon Creek has been on 303(d) list for fecal coliform and dissolved oxygen. It is recommended to monitor fecal coliform each month. Since DO is low during summer time when the temperature is high and most of the violations of temperature and DO take place during summer time, temperature and dissolved oxygen should be monitored during the months of May, June, July, August, and September. For the rest of the months, temperature should be monitored so that fecal coliform data can be thoroughly examined. For both of the creeks, turbidity and total suspended solids should be monitored during the months of November, December, January, February, March, April and May. Nutrients should be measured throughout the year.

Little Deep Creek and Deadman Creek are located near the downstream end of the Little Spokane River. Monitoring at the mouth of these two creeks will help to determine their effects on the mainstem of the Little Spokane River. Similarly to the above two creeks nitrate, phosphates, and fecal coliform should be monitored routinely. Turbidity should be monitored during the months of December, January, February and March. Dissolved oxygen and temperature should be monitored during summer time for Little Deep Creek. However, for Deadman Creek, monitoring is recommended on a year-round basis because the DO in the Creek has been severely low as seen in the study carried out by SCCD. Since dissolved oxygen concentrations are related to temperature, temperature should also be monitored continuously.

Moon Creek is located upstream of the Sacheen Lake while Buck Creek is located at the upstream of the Fan Lake. Monitoring stations at the mouths of the Moon Creek and Buck Creek will help to assess their contributing effects on the Sacheen Lake and Fan Lake, respectively. Similar to lakes, monitoring of pH, dissolved oxygen, nutrients, temperature, fecal coliform should be done regularly due to lack of data on these sites. Turbidity and total suspended solids should be measure at these points to identify the relative impacts of logging on Buck Creek.

Bear Creek was chosen as one of the sampling sites because it lies below the confluence of Eloika Lake and Dry Creek. Having a station at the mouth of the Beer Creek will provide an overall indication of water quality of West Branch and East Branch of the Little Spokane River. Similar to Dry Creek, it is recommended to monitor parameters regularly throughout the year. Since this creek lies at the middle of the mainstem of the Little Spokane River, turbidity should also be monitored at this station to assess if it is contributing to increases in turbidity downstream. As discussed in the historical data analysis, it has been noted that turbidity is high during winter. As a result of this we propose to monitor turbidity during the months of November, December, January, February, March, April and May.

Table 17. Summary of Proposed Monitoring Sites for TMDL Study

Station ID	Monitoring site	Continuous Stream Flow Monitoring Site	Location	Functions in the TMDL Sampling Design
1	Little Spokane River	Existing (LS-1)	Scotia Rd. near Newport	These three stations are located on main stream of Little Spokane River and the results of sampling should give an overall indication of water quality about the Little Spokane River. Station 1 and 4 are existing continuous stream flow operated by Spokane County Conservation and have some historical water quality observed data. Besides standard water quality parameters (Ammonia, Dissolved Oxygen, Fecal Coliform, Nitrate, pH, Phosphorus (Total and Ortho), Temperature, Total Suspended Solids, and Turbidity), some advanced water quality parameters (Carbamate Pesticides, Organophosphorus and Organonitrogen Pesticides, Herbicides) are also collected at these two stations in October 2004 and April 2005. These two periods are thought to coincide with pesticide/herbicide applications on agricultural lands in the watershed and thus represent the periods with the highest likelihood of detection. There is the possibility that some herbicides of concern will be used in August to help control Milfoil but predicting the exact residence time in the lakes is not possible at this time. Therefore, these two sampling events will be used. Station 3 used to be an Ecology station and was not sampled in 1990's. The sampling results give the overall water quality above Deadman.
2	Little Spokane River	Existing (LS-4)	Deer Park-Milan Rd. near Riverside	
3	Little Spokane River	No	Above Deadman Creek at 55B100 site	
4	Bear Creek	Proposed	At Highway 2	Bear Creek was chosen as one of the sampling sites because it lies below the confluence of Eloika Lake and Dry Creek. Similar to Dry Creek, it is recommended to monitor parameters regularly throughout the year. Since this creek lies at the middle of the mainstream of the Little Spokane River, turbidity should also be monitored at this station to assess if it is contributing to increases in turbidity downstream. As discussed in the historical data analysis, it has been noted that turbidity is high during winter. As a result of this we propose to monitor turbidity during the months of November, December, January, February, March, April and May.
	Beaver Creek	No	Near mouth	Beaver Creek is a tributary to the West Branch Little Spokane River. This

5				choice as one of the sampling sites can tell us how much it contributes to the West Branch water quality.
6	Buck Creek	Proposed	Near mouth	Buck Creek is also a tributary to the West Branch Little Spokane River. The 303 (d) was listed the area below the confluence of Buck Creek and West Branch. The results can tell us whether the Buck Creek contribute to these 303(d) lists or not.
7	Dartford Creek	Proposed	Near mouth	Dartford Creek flows into main channel of Little Spokane River and unfortunately 303(d) were in the listed for the channel session where the Dartford Creek joins the main stream. The site will help us to determine how much it contributes to the main stream. A continuous gage was proposed in order to run water quality model.
8	Deadman Creek	Existing	15628 N. Little Spokane Drive in Spokane	Deadman Creek are located near the downstream end of the Little Spokane River and is listed on the 303(d). Monitoring at the mouth of Deadman Creek will help to determine their effects on the mainstream of the Little Spokane River. The nitrate, phosphates, and fecal coliform should be monitored routinely. Turbidity should be monitored during the months of December, January, February and March. Dissolved oxygen and temperature should be monitored during summer time for Little Deep Creek. However, monitoring is recommended on a year-round basis because the DO in the Creek has been severely low as seen in the study carried out by SCCD. Since dissolved oxygen concentrations are related to temperature, temperature should also be monitored continuously. Besides, Station 8 is also chosen as advanced water quality monitoring site.
9	Deadman Creek	No	Near confluence of Peone Creek	
10	Deer Creek	Proposed	Near mouth at Highway 2	Deer Creek watershed is also proposed as additional monitoring sites because they represent significant potential sources of flow and contaminants to the Little Spokane River. Nutrients, such as phosphate and nitrate, tend to increase as the river flows downstream. However, it is not clear whether the concentrations of the nutrient are higher in summer than in winter or vice versa. To assess this pattern we need to monitor nutrients routinely. Because of the lack of historical data, Deer Creek should be monitored for the same parameters as other watersheds in the basin

11	Dragoon Creek	No	Upstream of Deer Park	Dragoon Creek has been on 303(d) list for fecal coliform and dissolved oxygen. It is recommended to monitor fecal coliform each month. Since DO is low during summer time when the temperature is high and most of the violations of temperature and DO take place during summer time, temperature and dissolved oxygen should be monitored during the months of May, June, July, August, and September. For the rest of the months, temperature should be monitored so that fecal coliform data can be thoroughly examined. For both of the creeks, turbidity and total suspended solids should be monitored during the months of November, December, January, February, March, April and May. Nutrients should be measured throughout the year. Besides, Station 12 is also chosen as a advanced water quality monitoring site.
12	Dragoon Creek	No	Downstream of Dear Park	
13	Dragoon Creek	Existing	Crescent Rd. at Chattaroy	
14	Dragoon Creek (West Branch)	Proposed	West Branch of Dragoon at Parker Road	
15	Dry Creek	Proposed	Near mouth at Milan-Elk Road	Monitoring near the mouth of the Dry Creek should be done to evaluate if land use practices in that watershed are contributing to pollution in the mainstem of the Little Spokane River. Since no historical record was found on this site, the monitoring of pH, dissolved oxygen, temperature, fecal coliform, and nutrients should be done routinely throughout the whole year. Turbidity and suspended solids should also be measured.
16	Little Deep Creek	Proposed	Near mouth at Shady Slope Road	Little Deep Creek is located near the downstream end of the Little Spokane River. Monitoring at the mouth of it will help to determine its contribution to the mainstream water quality of the Little Spokane River. The nitrate, phosphates, and fecal coliform should be monitored routinely. Turbidity should be monitored during the months of December, January, February and March. Dissolved oxygen and temperature should be monitored during summer time for Little Deep Creek.
17	Moon Creek	Proposed	Upstream of Sacheen Lake	Moon Creek is located upstream of the Sacheen Lake while Buck Creek is located at the upstream of the Fan Lake. Monitoring stations at the mouths of the Moon Creek and Buck Creek will help to assess their contributing effects on the Sacheen Lake and Fan Lake, respectively. Similar to lakes, monitoring of pH, dissolved oxygen, nutrients, temperature, fecal coliform should be done regularly due to lack of data on these sites. Turbidity and total suspended solids should be measure at these points to identify the relative

				impacts of logging on Buck Creek.
18	Otter Creek	Existing	Elk to Highway Road near Elk	Otter Creek is located in the junction of West Branch Little Spokane River and upstream of Little Spokane River. Both West Branch and upstream of Little Spokane were listed on 303(d), but Otter is not there. We don't know whether it is because of no historical data or its water quality meets the standards. Besides, there is a continuous flow gage operated by SCCD.
19	Peone Creek	No	Upstream confluence of Deadman Creek	Peone Creek is a tributary of Deadman Creek. The site helps us to determine how much it contributes to the water quality issue for Deadman, where there is a 303(d) problem.
20	West Branch Little Spokane River	No	Downstream of Sacheen Lake	It is located at the outlet of Sacheen Lake. The sampling results at this site will give us the water quality about the Sccheen Lake, which is on the 303(d) as Category 5. The advanced water quality parameters also analyzed at this site, because the water quality at Sacheen Lake is really concerned.
21	Little Spokane River	No	Indian Trail Road crossing	It is located near the mouth of Little Spokane River. There are great amount of groundwater discharge to mainstream of Little Spokane River and sampling at this site can reflect groundwater's effects.
22	West Branch Little Spokane River	Proposed	Upstream Eloika Lake at Allen Road West	It is located at upstream of Eloika Lake. It gives the background information about the water quality into the Elokia Lake. A continuous gage was proposed to run water quality model for TMDL study and this site is also an advance water quality parameter site.
23	West Branch Little Spokane River	Proposed	Near mouth at Highway 2	It is located at the mouth of West Branch Little Spokane River and should give overall water quality about the West Branch Little Spokane, which is the really important tributary of Little Spokane River, the home of a quite number of Lakes, and major sources of water for main channel. Because of these, a continuous gage was proposed at this site and advanced water quality parameters were analyzed at this site.
24	Urban Runoff	No	Pine River Park	These two sites are located at south banks of Little Spokane River and in the Urban zones. The major reasons having sits here are to study the impacts of urbanization on water quality. Station 24 is also served as an advanced water quality site.
25	Urban Runoff	No	Waikiki Springs	

Another consideration is that Category 1 streams and rivers meet existing water quality standards. Table 18 contains a summary of the major sub-watersheds and lists those where water quality information has demonstrated that the waterbodies meet current standards. It is important to note that the stream segment (e.g., sampling location) is an important consideration. Some streams are listed as both areas of concern and areas that meet water quality criteria simply because the upper segments may have better water quality or cooler temperatures than segments closer to the mouth of the stream. For example, dissolved oxygen is a parameter of concern on Dragoon Creek (Table 16) but Dragoon Creek is also listed as a stream where DO meets existing criteria (Table 18).

Table 18. Little Spokane River Basin Stream Segments Meeting Requirements

Stream	Parameter
Bear Creek	--
Dartford Creek	--
Deadman (Peone) Creek	Ammonia, Dissolved oxygen
Deer Creek	Dissolved oxygen, Fecal coliform, pH, Temperature
Dragoon Creek	Ammonia, Dissolved oxygen
Dry Creek	--
Little Deep Creek	--
Little Spokane River	Ammonia, Dissolved oxygen, Fecal coliform, pH
Otter Creek	--
West Branch Little Spokane River	--

6.2 Lake Segments of Interest

The Little Spokane watershed, particularly in the West Branch of the Little Spokane River drainage, has a number of small to medium size lakes that are important features in the basin. The lakes provide recreational areas that are popular to the area residents. Table 19 identifies the significant lake segments in the watershed. Sacheen Lake is the only lake currently listed as a Category 5 waterbody, however, many of the other lakes are listed as Category 2. Table 20 indicates the parameters of concern. A preliminary study done by the POCD has shown that Eloika Lake violated temperature and dissolved oxygen criteria at least on one occasion. According to the water quality assessment carried out by Ecology, stratification was not seen in Eloika Lake and Diamond Lake (Ecology, 1994) while Horseshoe Lake mostly had oxygenated hypolimnion (Ecology, 1998). Because the lake is impaired, outflows could have an adverse effect on downstream water quality. As historical information on the other lakes is not readily available, it is impossible to determine whether water quality criteria violations have occurred in the lakes or whether there have been adverse effects downstream. Table 21 documents those lake segments that currently meet State standards for the parameters sampled.

Table 19. Little Spokane River Basin Lake Segments of Interest

Waterbody	303(d) status
Bear Lake	Yes – 2
Chain Lake	Yes – 2
Eloika Lake	Yes – 2
Fan Lake	Yes – 2
Reflection Lake	Yes – 2
Sacheen Lake	Yes – 5
Trout Lake	Yes - 2

Table 20. Listed Lake Segment Parameters

Stream	Listed Category 5 Parameters	Listed Category 2 Parameters
Bear Lake	--	Total Phosphorus
Chain Lake	--	Total Phosphorus
Eloika Lake	--	Total Phosphorus
Fan Lake	--	Total Phosphorus
Reflection Lake	--	Total Phosphorus
Sacheen Lake	Fecal Coliform, Total Phosphorus	
Trout Lake	--	Total Phosphorus

Table 21. Little Spokane River Basin Lake Segments Meeting Requirements

Stream	Parameter
Diamond Lake	Total Phosphorus
Horseshoe Lake	Fecal Coliform
Sacheen Lake	Total Phosphorus

Sampling of individual lakes, while important for fecal coliform and temperature considerations, was deemed outside the scope of the current monitoring plan. Inferences to lake water quality will be made by sampling upstream and downstream of several lakes. To help address the concerns of local residents regarding the use of chemicals to control Milfoil in the lakes, herbicide samples will be collected at nine stream locations around the basin. This is a screening level analysis only. It is not for TMDL analysis at the present time.

6.3 Proposed Sampling Parameters and Locations

In addition to the parameters already identified, stakeholders were also concerned about their potential exposure to pesticides. To help alleviate or validate these concerns, three categories of pesticides will be examined on a semi-annual basis. With these additions, Table 22 summarizes the complete list of parameters that will be monitored. The list is comprised of three categories: flow, standard water quality parameters, and advanced water quality parameters. Based on the stream flow summary in Chapter 2, it is recommended that 10 additional stations be added to collect continuous flow information. Table 23 identifies the streams and possible locations. Each of these locations would also represent a water quality sampling location. Staff gages would be installed at the other 15 water quality sampling locations so that instantaneous flow measurements can be obtained in a manner consistent with that used by the SCCD at its current sites. This procedure is outlined in the "Methods" section of this report. The ten proposed continuous stream flow locations listed in Table 23 represent locations at or near the mouths of all significant tributaries in the watershed plus a couple of other important locations. The spatial coverage provided by these locations are shown in Figure 27.

To effectively develop TMDLs, it is essential to locate new monitoring sites as well as operate old monitoring sites on a continuous basis. Based on the data gap analysis and assuming that existing monitoring at 55B070 will continue, the monitoring sites identified in Table 24 are proposed. Overall, twenty-five sites will be sampled either discretely or continuously depending on the parameter and location.

Table 22. Sampling Parameters

Category	Parameter
Flow	Continuous Discharge Instantaneous Discharge
Standard Water Quality Parameters	Ammonia Dissolved Oxygen Fecal Coliform Nitrate pH Phosphorus (total) Temperature Total Suspended Solids Turbidity
Advanced Water Quality Parameters	Carbamate Pesticides Organophosphorus & Organonitrogen Pesticides Herbicides

The advanced water quality parameters are being collected for screening level analysis to determine if potential problems exist from pesticide/herbicide use around the basin including but not limited to Milfoil eradication. Four different types of herbicides: 2,4_D Granular, Diquat, Endothall, and Fluridoe have been used to control Milfoil in the watershed. Monitoring of the

herbicides will be done not only at the lakes, but also at other locations around the Little Spokane River as listed in Table 25. With the current budget it is not feasible to perform test for all of these herbicides. As a result, only the herbicide (2,4_D) that is prominently used will be tested.

Table 23. Proposed Stream Gaging Locations

Stream	Location
Bear Creek	At Highway 2
Buck Creek	Near mouth
Dartford Creek	Near mouth
Deer Creek	Near mouth at Highway 2
Dragoon Creek	West Branch of Dragoon at Parker Road
Dry Creek	Near mouth at Milan-Elk Road
Little Deep Creek	Near mouth at Shady Slope Road
Moon Creek	Upstream of Sacheen Lake
West Branch Little Spokane River	1. Near mouth at Highway 2 2. Upstream Eloika Lake at Allen Road West

Table 24. Proposed Monitoring Sites for Standard Water Quality Parameters

Station ID	Monitoring site	Continuous Stream Flow Monitoring Site	Location
1	Little Spokane River	Existing (LS-1)	Scotia Rd. near Newport
2	Little Spokane River	Existing (LS-4)	Deer Park-Milan Rd. near Riverside
3	Little Spokane River	No	Above Deadman Creek below LSR Dr.
4	Bear Creek	Yes - WSU	Near Findley Road
5	Beaver Creek	No	Below Horseshoe Lake
6	Buck Creek	Yes - WSU	Above Horseshoe Lake
7	Dartford Creek	Yes - WSU	At Hazard Rd. near Dartford, WA.
8	Deadman Creek	Existing (LS-6)	15628 N. Little Spokane Drive in Spokane
9	Deadman Creek	No	At Heglar Rd.
10	Deer Creek	Yes - WSU	Near mouth at Highway 2
11	Dragoon Creek	No	At Dahl Rd. upstream of Deer Park
12	Dragoon Creek	No	At Monroe Rd. below Deer Park
13	Dragoon Creek	Existing (LS-5)	Crescent Rd. at Chattaroy
14	Dragoon Creek (West Branch)	Yes - WSU	West Branch of Dragoon at Monroe Rd.
15	Dry Creek	Yes - WSU	Near mouth at Milan-Elk Road
16	Little Deep Creek	Yes - WSU	Near mouth at Shady Slope Road
17	Moon Creek	Yes - WSU	Upstream of Sacheen Lake
18	Otter Creek	Existing (LS-3)	Elk to Highway Road near Elk
19	Peone Creek	No	Upstream confluence of Deadman Creek
20	West Branch Little Spokane River	No	Downstream of Sacheen Lake
21	Little Spokane River	No	Indian Trail Road crossing
22	West Branch Little Spokane River	Yes - WSU	Upstream Eloika Lake at Allen Road West
23	West Branch Little Spokane River	Yes - WSU	Near mouth at Highway 2
24	Urban Runoff	No	Pine River Park
25	Urban Runoff	No	Waikiki Springs

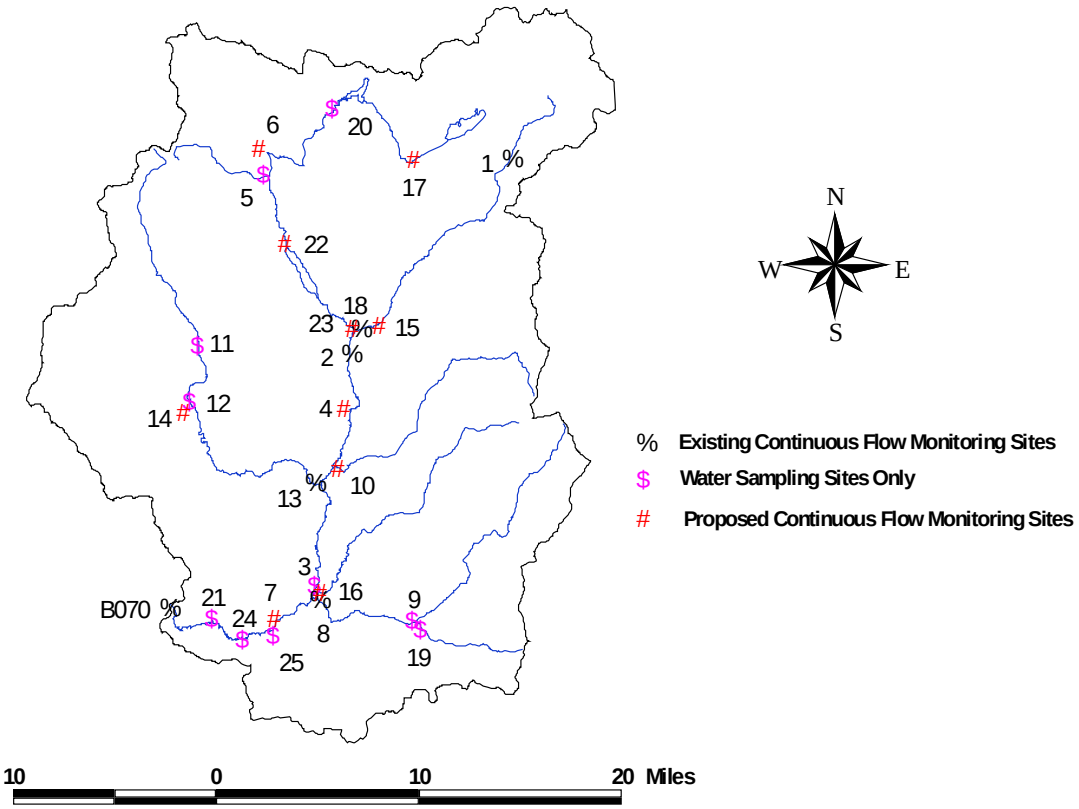


Figure 27. Sampling Locations for Standard Water Quality Parameters

Because of the analytical expense associated with herbicides and pesticides, there are fewer locations where these samples will be collected. Table 25 contains the locations of the sites. The spatial coverage of these locations is shown in Figure 28.

Table 25. Proposed Monitoring Sites for Advanced Water Quality Parameters

Station ID	Monitoring site	Continuous Flow Monitoring Site	Location
1	Little Spokane River	Existing (LS-1)	Scotia Rd. near Newport
2	Little Spokane River	Existing (LS-4)	Deer Park-Milan Rd. near Riverside
26	Little Spokane River	No	Near mouth at 55B070 location
8	Deadman Creek	Existing	15628 N. Little Spokane Drive in Spokane
12	Dragoon Creek	No	Downstream of Dear Park
20	West Branch Little Spokane River	No	Downstream of Sacheen Lake
22	West Branch Little Spokane River	Proposed	Upstream Eloika Lake at Allen Road West
23	West Branch Little Spokane River	Proposed	Near mouth at Highway 2
24	Urban Runoff	No	Pine River Park

6.4 Proposed Monitoring Schedule

The water quality monitoring plan includes both a long-term routine sampling strategy and a short-term intense monitoring phase. For the long-term plan, the standard water quality parameters listed in Table 22 will be collected on a monthly basis during 15 months, including 12 consecutive months beginning in January 2005. Late in the initial 12 month phase, discussions amongst the involved parties will determine if the final 3 months of sampling should begin in January 2006, or be 'delayed' to a timeline including spring runoff conditions (e.g. March-May). The first 12 months will be used as calibration data for the prediction models. The last 3 months will be used for validation of the models.

The advanced water quality parameters listed in Table 22 will be sampled in May and October 2005. These two periods are thought to coincide with pesticide/herbicide applications on agricultural lands in the watershed and thus represent the periods with the highest likelihood of detection. There is the possibility that some herbicides of concern will be used in July to help control Milfoil but predicting the exact residence time in the lakes is not possible at this time. Therefore, these two sampling events will be used.

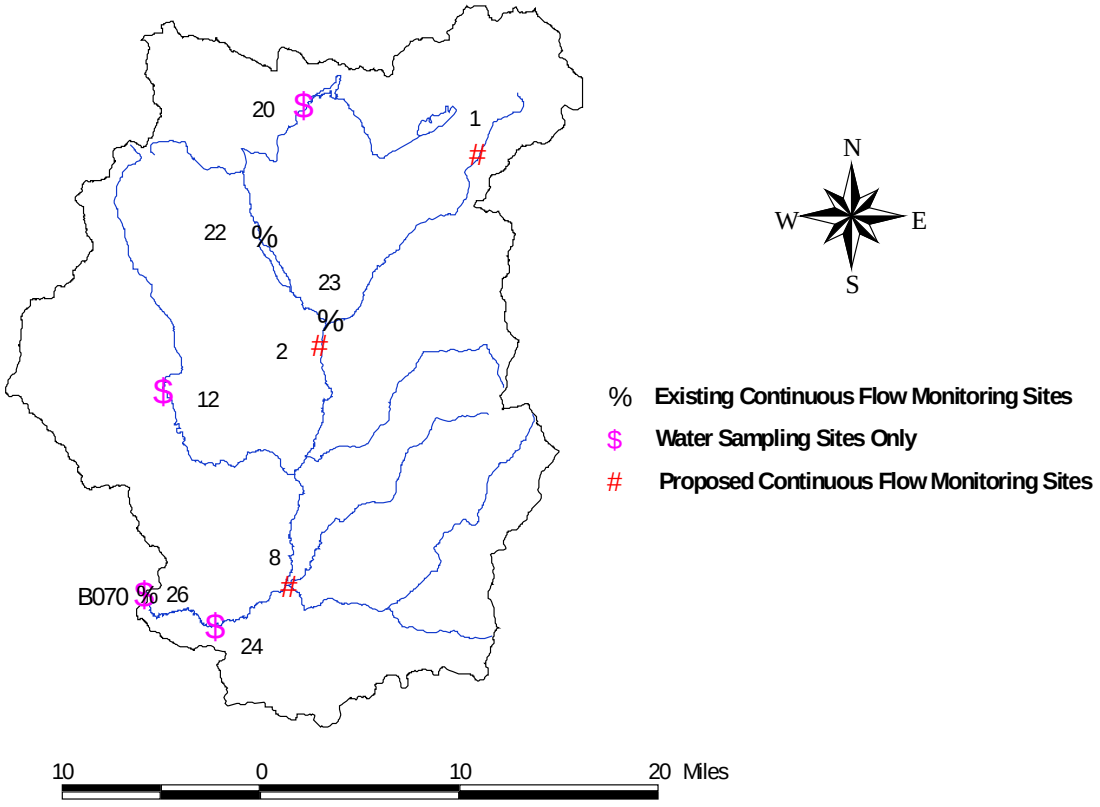


Figure 28. Sampling Locations for Advanced Water Quality Parameters

6.5 Additional Water Quality Sampling Activities

Additional short-term sampling events will be conducted to help gage stormwater runoff impacts and for specific model calibration and validation purposes. These including sampling of flow and sediments during storm events, and continuous monitoring of diel dissolved oxygen and pH changes during hot clear summer days.

Storm event sampling will be conducted at existing monitoring sites where representative pollutant loading from storm water runoff is expected, and where discharge measurements are possible. Storm sampling locations will be representative of land uses observed throughout the watershed, and will include urban, forested, and agricultural land areas.

Three storm sampling events will be conducted representing the early, middle, and late portions of the rainy season (November-June). To the degree that seasonal weather patterns, predictability and other logistic constraints allow, the storm events most likely to produce

sediments, such as rain on frozen soil will be selected for sampling. One to two sites will be sampled from each land use category during each storm sampling event; specific numbers of sites sampled within each category/event may be weather dependent (e.g. if storm events are localized in nature some sites may not be effected/sampled). Forested and urban areas within the Little Spokane watershed typically represent subwatersheds with relatively uniform land cover; representative (single) samples will be collected to evaluate the storm runoff generated from these areas. In contrast, agricultural areas tend to lie within the central portions of the watershed with other land uses (e.g. forested) in upstream reaches; paired (upstream/downstream) samples will be collected to evaluate the storm runoff generated specifically from agricultural areas.

Grab samples will be taken during a prolonged storm event, or shortly after a significant short-term storm event. A notable visual increase in the color/turbidity of the streamflow relative to typical conditions will be taken as an indicator that a storm event is influencing stream (and potential pollutant) runoff at the time of sampling. The storm samples will be analyzed for TSS, TP, and coliform concentrations. The information on the time of the sampling and the sediment concentrations will allow the project team to construct a sediment-loading graph. Such data, when is related to the land use of the upstream watershed, can be used for estimating the contribution of the sediment sources. Additionally, the data can also be used to calibrate the model used for load allocation, and to verify the load allocated.

The diel DO and pH sampling will be conducted at six sites throughout the watershed where high temperatures and low DO concentrations have been identified. Data gathered during diel monitoring efforts will be used for the purpose of both model calibration and load allocation verification. Diel monitoring sites will include:

- Site 2 – Little Spokane River at Deer Park-Milan Rd.
- Site 3 – Little Spokane River at Little Spokane River Drive above Deadman Ck.
- Site 8 – Deadman Creek near Little Spokane River Drive.
- Site 13 – Dragoon Creek at Crescent Rd.
- Site 23 – West Branch Little Spokane River below Eloika Lake.
- Site 26 – Little Spokane River near mouth at Ecology station 55B070.

As DO is inversely related to temperature, sampling will be conducted in the summer time (early September). Attempts will be made to schedule diel monitoring on clear days when maximum sunlight will stimulate the highest algal production activity. High temperatures and clear days will represent the worst-case scenario of low DOs during night and high pH changes between day and night.

Hydrolab or MP Troll multi-parameter water quality probes will be utilized to log diel water quality parameters; Temperature, DO, pH, and conductivity will be logged at 15 minute intervals for 2 consecutive days at each selected site. Due to limited availability of multi-parameter data loggers, sites will be monitored in stages. Sites 3, 8 and 26 will be monitored initially for 2 consecutive days; available data loggers will then be moved and sites 2, 13, 23 and 26 will be monitored for 2 consecutive days. Site 26 will be monitored during both stages to provide an overview of any relevant changes in water quality trends or measures that may differ between monitoring stages.

Coincidentally with diel monitoring activities at each site, two water grab samples will be collected at times expected to correspond with daily high and low DO levels. Water quality grab samples will be analyzed for nitrogen (Nitrate, Nitrate/Nitrite, Nitrite, Total Kjeldahl, and Organic), Phosphorous (total and orthophosphate), pH, TSS, and turbidity.

Temperature modeling will also require the estimation of canopy cover and local streambank topographic shade. Canopy cover (density, overhang, and tree height) will be measured at increments along the streams as necessary to account for variations in riparian characteristics. A solar pathfinder will be used to map density during the July-September window corresponding to high water temperatures. Overhang will be measured with a tape measure. Tree height will be determined using a clinometer. Site locations for measuring the effective shade will be selected randomly from a subset of representative vegetation polygons to provide a statistically-based shade value for each vegetation type. Two Davis weather stations will be deployed during this study to record wind, solar, and relative humidity data necessary for accurate temperature modeling.

Groundwater inflow to the river is expected to play a major role in mitigating stream temperature; especially in the lower reaches of the Little Spokane River. During low flow conditions, stream gaging will be conducted at multiple transects along the lower LSR and the major tributaries. This gaging effort will be conducted over as short a time frame as logistically possible to insure that fluctuations in seepage rates are minimized.

For the stream reaches where TMDL development is required, all major point sources will be evaluated. First, estimations will be made based on the size, nature, and characteristics of the point source. Second, the records of the 13 sites identified in Table 7 as required by the NPDES permit will be reviewed. We will investigate to determine whether the site is monitored by other means, such as EPA, Ecology, or SCCD. If so, we will contact with them and to get the monitoring results. If the data is considered not adequate, additional monitoring will be conducted. If the point sources are self-monitoring, a few replicate samples will be collected to address QA concerns. If the site isn't being monitored, the reason will be stated. In case where the reason is that they don't have a direct discharge or they are not a significant source, evidence will be supplied. The monitoring data will be used to assess the contribution of the point source and to verify proposed load allocations.

7 METHODS

This chapter summarizes the methods that will be used to collect the data needed for the project such that consistent, reliable results can be obtained.

7.1 Flows

Although strictly speaking, flow measurement comes under the heading of physical parameter rather than water quality, it is often necessary to have discharge measurements at the same general sample locations in order to calculate loads and interpret changes in pollutant concentrations. The USGS has a single gage currently in operation within the LSR watershed. The SCCD operates an additional five stations. In November/December of 2004, WSU installed staff gages and continuous flow recorders at ten additional locations as part of this data collection effort (See Table 24). The recorders are actually self-contained pressure transducers and loggers that record the water depth at user-defined intervals. The ten new installations consist of the Water Level Logger (WL15) from Global Water Instrumentation. This instrument records pressure (water stage) at a user-defined time interval. A correlation between flow and water depth called a "rating curve" (aka stage-discharge relationship) is established from measured data. As shown in Figure 29, the standard unit consists of a pressure transducer, 25-feet of cable, and a data logger. The unit fits inside a 2-inch PVC housing for easy installation (also shown in Figure 29). The basic WL15 unit comes with a 9V lithium battery good for up to 3 years depending on recording frequency. At 30-minute intervals the theoretical battery life is 424 days but the battery will be checked every 3 months and replaced as necessary. The data will be downloaded to a PC with software and cables supplied with the unit.

Instantaneous flow estimates will be taken at the other ten locations during water quality sampling events. The method adopted by the SCCD is to calibrate a staff gage (or similar device to monitor depth) to flow by measuring the discharge and computing Manning's roughness value for a particular reach.

This is done by measuring discharge and cross-section geometry at the sampling location during the initial sampling event. Then, this information is substituted into Manning's Equation:

$$Q = \frac{1.49}{n} A R^{2/3} S^{1/2}$$

where n is the Manning's roughness, A is the cross-sectional area (ft^2), R is the hydraulic radius (area divided by wetted perimeter), and S is the longitudinal bed slope. Because Q, A, R, and S are known, the roughness coefficient can be determined. On subsequent visits, by recording the depth at the staff gage, a quick estimate of the discharge can be made.

The advantages of using this method and a staff gage are lower initial costs and the relative speed at which flow estimates can be made. The disadvantage is that are that Manning's roughness is not necessarily constant with flow so estimate errors are possible. Furthermore, since someone has to read the stage, continuous monitoring is not feasible. Consequently, the

impacts of storm events on water quality parameters may be more difficult to track. Even diurnal fluctuations will most likely be missed.

Flow data will be collected during 15 months with initial data collection from December 2004 through December 2005. Additional flow measurements will be conducted during 3 subsequent but unspecified months (Refer to Section 6.4, paragraph 1 for an overview of sampling timelines). Instantaneous flows will be measured at tributary sites when samples are taken by measuring velocities with a Price or Pygmy current meter at sixteen or more divisions of a cross-section (WAS, 1993). If channels are small, velocities will be measured at as many divisions as practical given restrictions (e.g. width) of the measuring device.

Figure 29. Global Water Pressure Transducer and Logger

7.2 Temperature

Water temperature at the field sites is an essential water quality parameter and will be measured at all sampling locations. There are several techniques commonly used to record temperatures. Table 26 summarizes the typical temperature sensor and their accuracy.

Temperatures will be measured with either a thermistor or thermometer during all standard sampling events. Thermistors or thermometers will be calibrated or checked for accuracy according to manufacturers instructions prior to each sampling event. Temperature will be measured in those sections of the stream that represent most of the water flowing in a reach. The sensor will be immersed in the water to the correct depth and held there for no less than 5 minutes until the sensor equilibrates thermally. Temperature will be recorded to the nearest 0.5°C or less if appropriate (e.g. 0.1°C for many thermistor readings).

Table 26. Summary of Temperature Equipment

Equipment	Accuracy	Reporting Limit
Certified Reference Thermometer/ # 61099-035, HB Instrument Co.	0.1 °C	0.1 °C
Field Thermometer/ # 1546RL, Brooklyn Thermometer Co.,	0.2 °C	0.1 °C
Thermistor Thermometer/ #U-08402 Thermistor & #U-93823 Probe, Cole Parmer Co.,	0.3 °C	0.1 °C
Temperature Logger (Water/Air) #TBI 32-05+37 StowAway TidbiT, Onset Computer Corp.	0.2 °C	0.1 °C
Temperature Logger (Air) #TBI 32-20+70 StowAway TidbiT, Onset Computer Corp.	0.2 °C	0.1 °C

A complete list of activities and supplies needed for temperature measurement is presented in Table 27. Several activities, such as determining the number of stations or determining the deployment schedule, are performed only once before the sampling has actually begun. Others need to be considered each month.

As indicated in Table 26, ONSET Computer Corporation (http://www.onsetcomp.com/) manufactures relatively economical temperature loggers that have proven to be reasonably accurate. Their product line includes several temperature probes. The Onset Hobo Water Temp Pro is perhaps the simplest choice for stream environments. As illustrated in Figure 30, the entire unit is approximately 5" long x 1.2" in diameter and weighs 1.5 oz. It has a user-definable sampling interval ranging from 1 second up to 9 hours. At 30-minute intervals (48 samples per day), the basic unit can easily store several months worth of data. However, for this project, temperature will be recorded at 15-minute intervals and the data will be downloaded monthly.

The instrument, calibration check, deployment procedures, mid-deployment check, retrieval check, downloading procedure, and quality control procedures are based on “Continuous Temperature Sampling Protocols for the Environmental Monitoring and Trends Section” by Department of Ecology (Publication No. 03-03-052).

Table 27. Continuous Temperature Sampling Checklist

Pre-Deployment Preparation	**Van/Safety Equipment**
Determine Number of Stations Determine Deployment Equipment Needs Obtain or Make Deployment Equipment Check Calibration of: • Temperature Loggers • Thermometer • Thermistor Plan Deployment Schedule Schedule Field Assistance Program Temperature Loggers Make Motel Reservations Fill out Field Work Plan and Contact Person Designation Form Gas Van	Tire Chains Yellow Hazard Beacon Flashlight Tool Chest Jumper Cables Flares/Reflectors First Aid Kit Foil Blanket Orange Vests 2 Gallons Drinking Water Hand Towels
Sampling Equipment and Supplies	**Personal Gear**
Programmed Temperature Loggers Continuous Temperature Survey Forms Thermometer Thermistor Compass Maps Watch Camouflaged PVC Pipe Cable Ties Rebar Pounder 3/8 inch x 2 – 3 Ft. Rebar Pieces 4# Hammer Several lengths of Chain Pyramid Blocks Small Wire Cutters 6’ Pole W/Hook Knife Hand Trimmer Machete Survey Flagging Digital Camera GPS	Rain Gear Knee Boots Waders Gloves Extra Clothing Hat

Figure 30. Continuous Temperature Measurement Sensor

7.3 Sample Collection and Field Measurement Methods

The procedures described in the *National Field Manual for the Collection of Water-Quality Data* (Franceska et al 1998) from USGS will be used for *in situ* parameter measurement, sample collection, preservation, and shipping of samples to the Water Quality Laboratory at Washington State University.

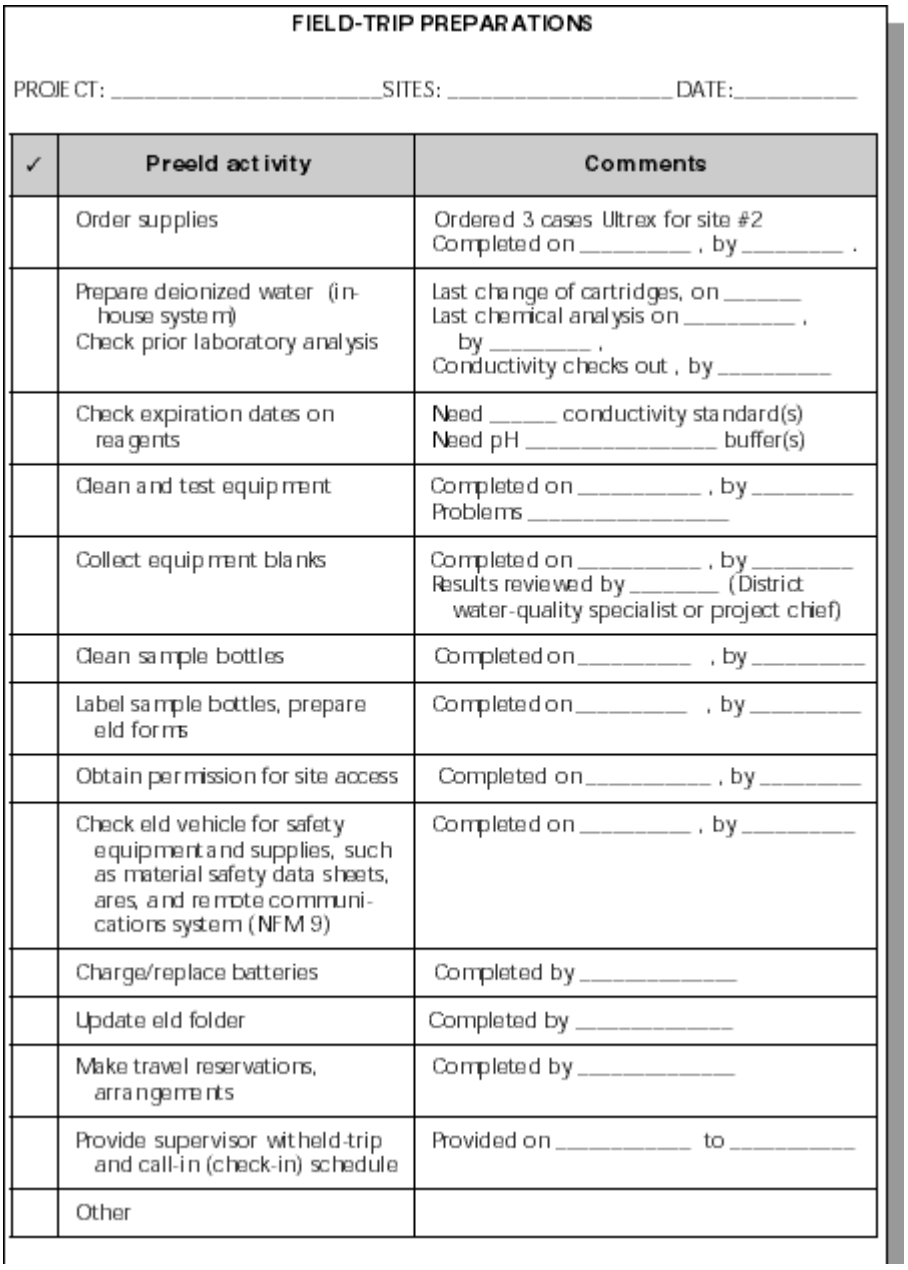
7.3.1 Preparations for Water Sampling

Preparations for water quality sampling include field-trip preparations (such as, selection of sample-collection sites, site reconnaissance, and vehicle preparation), equipment preparation (such as equipment calibration, equipment clearing, sample bottle, and battery charges or replacements), and supplies preparations (such as safe equipment, note book, clothes). A general checklist, such as the one presented in Table 28, is helpful at this stage. A specific checklist, similar to the one from the *National Field Manual for the Collection of Water-Quality Data* and shown as an example in Figure 31, will also be used for planning each trip.

Table 28. Preparation of field trip

Types of information	Examples of items or activities in checklists
Calendar of planned field trips	Prepare calendars/checklists that include sampling dates, members of field team, vehicle(s) to be used.
Presampling activities	Prepare checklists; for example, field-trip preparations checklist and well- information checklist.
Postsampling activities	Update field folders and computer files. Log in samples (Analytical Services Request form). Store and dispose of hazardous materials properly. Check that all equipment is clean and properly stored.
Field equipment and supplies	Prepare lists of equipment/supplies for each field site (see NFM 2). Prepare a list of items to be ordered.
Equipment/supplies maintenance and testing	Prepare a checklist of maintenance/testing for field-measurement instruments (see NFM 6). Test sample-collection and processing equipment. Charge or replace batteries.
Vehicle maintenance	Check fluids, battery, tires, lights, cleanliness.
Sample-collection, -processing, -shipping, and -documentation information and supplies	Prepare headers on forms (such as field, chain-of-custody, and Analytical Services Request forms); prepare bottle labels. Prepare lists of chemical constituents, with analytical schedules, methods, laboratory codes; bottle type and volume; sample handling, treatment, and preservation procedures; shipment; quality-control samples.
Field-folder contents	Prepare list of logistical information needed for each site, such as permission to access site, keys, maps.
Safety equipment and information	Keep a copy of NFM 9 for field use and list special considerations for the site, such as personal flotation devices.

Figure 31. An example of a pre-sampling activities checklist



FIELD-TRIP PREPARATIONS

PROJECT: _____ SITES: _____ DATE: _____

✓	Preeld activity	Comments
	Order supplies	Ordered 3 cases Ultrex for site #2 Completed on _____ , by _____ .
	Prepare deionized water (in-house system) Check prior laboratory analysis	Last change of cartridges, on _____ Last chemical analysis on _____ , by _____ , Conductivity checks out , by _____
	Check expiration dates on reagents	Need _____ conductivity standard(s) Need pH _____ buffer(s)
	Clean and test equipment	Completed on _____ , by _____ Problems _____
	Collect equipment blanks	Completed on _____ , by _____ Results reviewed by _____ (District water-quality specialist or project chief)
	Clean sample bottles	Completed on _____ , by _____
	Label sample bottles, prepare eld forms	Completed on _____ , by _____
	Obtain permission for site access	Completed on _____ , by _____
	Check eld vehicle for safety equipment and supplies, such as material safety data sheets, ares, and remote communi-cations system (NFM 9)	Completed on _____ , by _____
	Charge/replace batteries	Completed by _____
	Update eld folder	Completed by _____
	Make travel reservations, arrangements	Completed by _____
	Provide supervisor with eld-trip and call-in (check-in) schedule	Provided on _____ to _____
	Other	

7.3.2 *In Situ* Measurements

In situ measurements, made by immersing a field-measurement sensor directly in the water body, are used to determine a profile of variability across a stream section. *In situ* measurements are mandatory for determination of temperatures and dissolved-oxygen concentrations. Other properties such as pH, conductivity, and turbidity are often measured *in situ*, but may also be measured as a sub-sample of a composite sample collected using discharge-weighted methods.

Measurements made directly (*in situ*) in the surface- water body are preferable in order to avoid changes that result from removing a water sample from its source. In situ measurements are necessary to avoid changes in chemical properties of anoxic water. The measurements can be repeated if stream discharges are highly variable and measurement points need to be located at increments of equal discharge.

Accurate data on dissolved oxygen (DO) and pH levels in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Both DO and pH are typically measured In Situ. For this project, all DO measurements will be done via the amperometric method; pH measurements will be performed using the hydrogen ion electrode procedure. DO and pH measurements will be measured at mid-depth in the channel thalweg unless still-water or inadequate mixing conditions are present. In the case of still-water or inadequate mixing, DO and pH measurements will be taken from mid-depth at a central point in the channel.

DO and pH meters will be calibrated prior to each scheduled field sampling event according to manufacturers instructions. DO meters will be air-calibrated at each sampling site prior to taking stream measurements. To assess measurement accuracy during sampling, replicate DO and pH measurements of will be taken at randomly selected locations as described later in this document (see Section 7 - Quality Control Procedures).

7.3.3 Sample Collection Methods

In contrast to in situ measurements, many water quality parameters must be analyzed in the laboratory. In this case, samples will be collected, preserved as appropriate, and shipped back to a chosen laboratory for analysis.

Nutrient, sediment and turbidity samples will generally be obtained by the equal width increment (EWI) method to collect a sample volume proportional to the amount of flow at each of several equally spaced verticals in a cross section. This equal spacing between the verticals yields a gross sample volume proportional to the total streamflow. For streams over five feet wide, a minimum of 10 verticals will be used. For streams under five feet wide, as many verticals as practical will be used spaced at a minimum of six inches. In situations where limited stream depth, width or volume makes sampling via EWI methods impractical, grab samples will be taken in place of EWI samples.

EWI samples will be obtained using US Geological Survey US-DH-48, US DH-59, US DH-81 or US DH-84 standard depth-integrated samplers. The samplers use glass or polypropylene bottles of various sizes for sample collection, dependent upon the sampler used. Individual EWI sample bottles do not provide adequate volume for laboratory analyses required as part of this project. To achieve the necessary sample volumes for laboratory analyses, EWI sub-samples will be composited into 4-liter acid washed polypropylene bottles until adequate volume for all analyses has been achieved; the sample will be mixed thoroughly, and poured into appropriate containers as supplied by the receiving laboratory.

A clean (acid-washed) sample bottle will be used in the EWI sampler at each site sampled. Between sample sites, composite bottles and sampler nozzles, gaskets and vent tubes and will be rinsed thoroughly with deionized water.

Fecal coliform samples will be collected as grab samples using appropriately cleaned (autoclaved) containers supplied by the receiving laboratory. Samples are collected at the deepest swiftest portion of the cross section whenever possible to insure that stream properties are well mixed. Sample bottles will be inverted and submerged to approximately 6/10th the stream depth starting from the surface. At this point the bottle is uncapped and slowly turned upright with the mouth angled towards the direction of flow. The bottle is than capped under water immediately after becoming full and without retaining any air within the bottle.

7.3.4 General Field Procedures

EAP field methods will be followed for the collection of flow, dissolved oxygen, pH, temperature, and specific conductance, and for the deployment of data recording equipment (WAS, 1993). All sampling sites will have unique identification numbers. Field notes and field measurement data will be maintained in ink on water-resistant paper.

Field meter calibration will follow EAP protocols (WAS, 1993) under manufacturer's instructions. Calibration data will be recorded in the field notebooks. All water samples for laboratory analysis will be directly collected in pre-cleaned containers supplied by the Ecology-certified WSU laboratory or the ASL laboratory (pesticides/herbicides), except ortho-phosphorus and dissolved organic carbon, which will be collected in a syringe and filtered into a pre-cleaned container. The syringe will be rinsed with ambient water at each sampling site three times before filtering. Samples will be stored in the dark, on ice, and brought back to the WSU laboratory. Samples will be available at WSU for analysis within 30 hours of collection. When possible, bacteria and chlorophyll samples will be delivered for analysis within 24-hours of collection to avoid holding time violations.

Written land owner approval will be obtained prior to establishing precise monitoring locations. Copies of these permission letters will be provided to field personnel and taken on sampling trips as "proof" if questioned by neighbors. The Spokane County Conservation District (SCCD) will assist in obtaining land owner approval and finalizing site selection. In addition, the SCCD will participate in installing the field equipment, measuring stream flow, and collecting samples to help insure that data obtained are consistent with past collection efforts.

7.4 Laboratory Procedures

Laboratory analyses of other chemical parameters of interest listed in Table 29 will be performed in accordance with WSU Laboratory protocols (Chen 2004). Nutrient analyses will include inorganic (nitrate & nitrite, ammonia) forms of nitrogen, and total phosphorus. According to the WSU Laboratory manual (Chen 2004), the required reporting limits for laboratory data should be attainable through the analytical methods listed in Table 29. The WSU laboratory staff will

consult the project manager if any changes in procedures over the course of project are recommended, or if matrix difficulties are encountered. Field and laboratory equipment will be calibrated in accordance to the specifications spelled out in the laboratory QA/QC manual and summarized in Table 30. Relevant sample volumes, container requirements, and preservation techniques for samples to be analyzed in the laboratory are summarized in Table 31.

Sample quantities and processing procedures should not overwhelm the laboratory capacity. The project manager will follow normal procedures for notification and scheduling. If laboratory sample load capacities are in doubt, rescheduling of individual surveys may be negotiated. Storm-event surveys will require close communication with the laboratory to ensure microbiological media and other laboratory resources are available.

Table 29. Analysis Procedures for Water Quality Parameters

Sample Type	Parameters	Method	Lowest Detection Limit	Instruments
Water	Ammonia	EPA – 350.1	0.01 mg/L	OI Analytical FS3000
	Nitrate	EPA – 353.2	0.01 mg/L	OI Analytical FS3000
	Phosphorous	EPA – 365.1	0.01 mg/L	OI Analytical FS3000
	pH	APHA, 1998, 4500H^+-B	±0.02 pH unit prec., ±0.05 pH unit acc., report 0.1 pH unit	ACCUMET Portable AP5 pH meter
	Total Suspended Solids	APHA, 1998, 2540-D	1.0 mg/L	
	Fecal Coliform	APHA, 1998, 9222-D	1 coliform/100mL	
	Turbidity	APHA, 1998, 2130-B	0.05 NTU	Orbeco 965-10A

Table 30. Calibration Procedures and Frequency

Instrument	Time Interval	Specification
Analytical balance	Weekly	Calibration 0.1 mg derivation
pH meter	Upon use	Standardize with pH buffer 4.0, 7.0 and 10.0
Drying oven	Daily	Record temperature and adjust 103±0.5^{o}C
UV-Vis Spectrophotometer	Upon use	Set 0% absorbance and 100% T
Dissolved Oxygen Meter	Upon use	Winkler titration method

Table 31. Sample volumes, container requirements, and preservation techniques for samples collected for laboratory analysis.

Parameter	Volume	Container	Preservative	Holding Time
Fecal Coliform	200	Special	Sod. Thios.	6 Hours
Nitrogen				
Nitrate	200 ml	Plastic	Sulfuric	28 Days
Nitrate/Nitrite	100 ml	Plastic	Sulfuric	28 Days
Nitrite *	100 ml	Plastic	None	48 Hours
Total Kjeldahl	100 ml	Plastic	Sulfuric	28 Days
Organic	100 ml	Plastic	Sulfuric	28 Days
pH	100 ml	Plastic	None	Immediately
Phosphorus				
Total	50 ml	Plastic	Sulfuric	28 Days
Orthophosphate	50 ml	Plastic	Filt. Immed.	48 Hours
Specific Conductance	100 ml	Plastic	None	48 Hours
Total Suspended Solids	1 Liter	Plastic	None	7 Days
Turbidity	100 ml	Plastic	None	48 Hours

7.5 TMDL Modeling Approach

TMDL modeling and analysis will be performed using the water quality data collected in this study as calibration and validation information. TMDLs will be completed for:

1. Temperature
2. Fecal coliform bacteria
3. Phosphorus/TSS

Modeling approaches will be consistent with Ecology's standard practices. Coordination and cooperation with Ecology personnel will be maintained throughout the process to ensure results will be commensurate with their needs.

TTools, Shade Model, and QUAL2K models will be used to evaluate the loading capacity and to determine the wasteload and load allocations necessary to meet the water quality standards for temperature, fecal coliform, and phosphorus. TTools is an ArcView extension developed by Oregon Department of Environmental Quality (ODEQ, 2001) to develop GIS-based data from polygon coverages and grids. The tool determines vegetation and topography perpendicular to the stream channel and samples longitudinal stream channel characteristics, such as the near-stream disturbance zone and elevation.

The Shade model (Shade.xls) was adapted from a program originally developed by the Oregon Department of Environmental Quality (ODEQ) as part of the HeatSource model. Shade.xls calculates effective shade using one of two optional methods:

- ODEQ's original method from the HeatSource model version 7 (ODEQ, 2003).
- Chen's method based on the Fortran program HSPF SHADE (Chen, 1996).

QUAL2K (Q2K) is a steady-state river and stream water quality model that represents a modern version of the original QUAL2E model (Brown and Barnwell, 1987). QUAL2Kw is adapted from the Q2K model originally developed by Chapra (Chapra and Pelletier, 2003). Although QUAL2K requires steady-state hydraulic conditions, it can simulate diurnal heat budgets. The heat budget and temperature are simulated as functions of meteorology on a diurnal time scale. Consequently it is still a good model for TMDL temperature study. For the storm loads (unsteady flow conditions), HeatSource 7 will be used. Q2K is similar to QUAL2E in the following respects:

• *One Dimensional*. The channel is well-mixed vertically and laterally. Non-uniform, steady flow is simulated.
• *Diurnal Heat Budget*. The heat budget and temperature are simulated as a function of meteorology on a diurnal time scale.
• *Diurnal Water-Quality Kinetics*. All water quality variables are simulated on a diurnal time scale.
• *Heat and Mass Inputs*. Point and nonpoint loads and abstractions (withdrawals or losses) are simulated.

The QUAL2Kw framework includes the following new elements:

• *Software Environment and Interface*. Q2K is implemented within the Microsoft Windows environment. It is programmed in the Windows macro language: Visual Basic for Applications (VBA). Excel is used as the graphical user interface.
• *Model Segmentation*. Q2K can use either constant or varying segment lengths. In addition, multiple loadings and abstractions can be input to any reach.
• *Carbon Speciation*. Q2K uses two forms of carbon, rather than BOD, to represent organic carbon. These forms are a slowly oxidizing form (slow carbon) and a rapidly oxidizing form (fast carbon). In addition, non-living particulate organic matter (detritus) is simulated. This detrital material is composed of particulate carbon, nitrogen, and phosphorus in a fixed stoichiometry.
• *Anoxia*. Q2K accommodates anoxia by reducing oxidation reactions to zero at low oxygen levels. In addition, denitrification is modeled as a first-order reaction that becomes pronounced at low oxygen concentrations.
• *Sediment-Water Interactions*. Sediment-water fluxes of dissolved oxygen and nutrients from aerobic/anaerobic sediment diagenesis are simulated internally rather than being prescribed. That is, oxygen (SOD) and nutrient fluxes are simulated as a function of settling particulate organic matter, reactions within the sediments, and the concentrations of soluble forms in the overlying waters.
• *Bottom Algae*. The model explicitly simulates attached bottom algae.

• *Light Extinction*. Light extinction is calculated as a function of algae, detritus and inorganic solids.
• *pH*. Both alkalinity and total inorganic carbon are used to simulate pH.
• *Pathogens*. A generic pathogen is simulated. Pathogen removal is determined as a function of temperature, light, and settling.
• *Hyporheic Exchange and Sediment Pore Water Quality*. Q2K also has the ability to simulate the metabolism of heterotrophic bacteria in the hyporheic zone.

Table 32 contains the model parameters that need to be collected in order to run the HeatSource/Shadelator and Qual2k models for temperature. The data collection proposed as part of this project will assemble all of the pertinent information necessary to complete this task.

Table 32. Temperature model data requirements

		MODEL	
	PARAMETER	HeatSource/Shadealator	Qual2K
Flow	discharge - tributary	x	
	discharge (upstream and downstream)	x	
	flow velocity	x	
	groundwater inflow rate/discharge	x	
	travel time	x	
General	calendar day/date	x	x
	duration of simulation	x	x
	elevation-downstream	x	x
	elevation-upstream	x	x
	elevation/altitude	x	x
	latitude	x	x
	longitude	x	x
	time zone	x	
Physical	channel azimuth/stream aspect	x	
	cross-sectional area	x	x
	Manning's n value	x	x
	percent bedrock	x	x
	reach length	x	x
	stream bank slope	x	
	stream bed slope	x	x
	width-bankfull	x	
	width-stream	x	x
	temperature-groundwater	x	
	temperature-tributaries	x	
	temperature-water downstream	x	
	temperatures-water upstream	x	
	temperature-air	x	
Vegetation	% forest cover on each side	x	
	canopy-shading coefficient/veg density	x	
	diameter of shade-tree crowns	x	
	distance to shading vegetation	x	
	topographic shade angle	x	
	vegetation height	x	
	vegetation shade angle	x	
	vegetation width	x	
Weather	relative humidity	x	
	% possible sun/cloud cover	x	
	solar radiation	x	
	temperature-air	x	
	wind speed/velocity	x	

8 QUALITY CONTROL PROCEDURES

A comprehensive Quality Control and Quality Assurance procedures document has been developed for laboratory analysis procedures (Chen, 2004). The purpose of this quality assurance procedure is to summarize quality assurance (QA) and quality control (QC) activities designed to: 1) achieve quality goals desired for operation of the laboratory to ensure the data quality of the Little Spokane River TMDL project, 2) establish a set of operating principles that will constitute the quality-assurance program, and 3) identify standard operating procedures (SOP) for each analytical method, analyst training requirements, preventive maintenance on equipment, calibration procedures, corrective actions, internal quality control activities, performance audits, data assessment procedures for bias and precision, and data reduction procedures, validation processes, and reporting requirements.

It is also intended to give confidence to users of the lab's reports by listing specific methods and procedures by which the laboratory achieves its quality objectives. Quality assurance is important during sampling and transporting samples to the lab, while samples are being analyzed, and when data are reported. Because this is a laboratory accreditation program, the emphasis in reviewing the QA manual is on the analysis of samples and reporting of results, but documentation of sample and data management is also addressed. The QA manual is primarily intended for use by laboratory personnel to assure reliability of results. Secondarily, it will be used by personnel outside the laboratory to gain insight into and confidence in the overall QA measures used by the lab.

All analysts use some QC as an intuitive effort to produce credible results. However, a good quality control program consists of at least seven elements: certification of operator competence, recovery of known additions, analysis of externally supplied standards, analysis of reagent blanks, calibration with standards, analysis of duplicates, and maintenance of control charts. Details of these elements can be found in Chen (2004).

Table 33 contains a brief summary of QA/QC samples that will be used to assess data accuracy in both the laboratory and during field data collection. Field replicates used to assess various sources of data variability inherent in field collections; Table 34 summarizes the field parameters for which replicate sampling will be conducted in the field, the manner of replicate sampling (e.g. sequential vs. concurrent sample collection), and the source of variability being assessed by these samples. Additional detail regarding methods used to collect replicate samples for various parameters is provided in Appendix D.

Table 33. Summary of field and laboratory quality control procedures

Parameter	Field Blanks	Field Replicates	Lab Check Standard	Lab Method Bank	Lab Replicate	Matrix Spikes
Field Measurements						
Velocity/Flow*	n/a	1/run	n/a	n/a	n/a	n/a
Dissolved Oxygen	n/a	1/5 samples	n/a	n/a	n/a	n/a
pH	n/a	1/run	n/a	n/a	n/a	n/a
Temperature	n/a	1/run	n/a	n/a	n/a	n/a
Laboratory Analysis						
Ammonia	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/20 samples
Fecal Coliform	n/a	1/5 samples	n/a	1/run	1/run	n/a
Nitrate & Nitrite	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/20 samples
Phosphorus (total)	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/20 samples
TSS	1/survey	1/10 samples	n/a	1/run	1/10 samples	n/a
Turbidity	1/survey	1/10 samples	1/run	1/run	1/10 samples	n/a
Carbamate Pesticides	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/10 samples
Herbicides	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/10 samples
OP & ON Pesticides	1/survey	1/10 samples	1/run	1/run	1/10 samples	1/10 samples

* If the measured flow is within 5% of the expected flow from the existing rating curve, one flow velocity is enough. However, if it is not within the range, a replicate is needed.

Table 34. Summary of field replicate samples to be collected during TMDL sampling in the Little Spokane River

Parameter(s)	Manner of Collection	Variability Assessed and Collection Method
General Field Parameters – Temp., DO, pH	Sequential Sampling	Variability in field parameters during normal field sampling process (e.g. 1-2 hr. site visit). Record all general parameters upon arrival to the site; conduct all other sampling procedures; conduct replicate monitoring of general field parameters before leaving site.
Water Samples (For lab analysis)	Concurrent Sampling	Variability from sample collection, processing, handling and shipping. With EWI sampler – at each vertical collect a sub-sample and pour into a field-rinsed composite bottle. Resample the vertical and pour into a second composite bottle. When moving through transect verticals, alternate which composite bottle receives the first sub-sample collected. Grab samples – collect sample and replicate from same place in channel at as short of a time interval as is practical.
Flow	Sequential Sampling	Variability in field crew measurement, including that due to equipment. Establish transect and measure discharge, remove tape/line delineating transect, re-install tape/line delineating transect, measure (replicate) discharge.

8.1 Data Assessment Procedures and Reporting

Laboratory data reduction, review, and reporting will follow procedures outlined in WSU's QA/QC manual (Chen 2004). All water quality data will be entered into Ecology's Environmental Information Management (EIM) system. Data will be verified and 100% of the data entry will be reviewed for errors.

Elevated fecal coliform densities (> 200 cfu/100 mL) will be reported to the Ecology's Eastern Regional Office (ERO) in accordance with the official notification procedure. All other data will be made available to the ERO for disbursement after quality control and EIM are completed.

Data analysis will include evaluation of data distribution characteristics and, if necessary, appropriate distribution transformations. Estimation of univariate statistical parameters and graphical presentation of the data (box plots, time series, regressions) will be made using EXCEL or comparable computer software.

8.2 Data Quality Objectives

The decision whether to de-list or set TMDL targets on a water body for a particular parameter requires data adequate to reliability estimate the temporal and spatial variability of that parameter. Sampling, laboratory analysis, and data evaluation steps have several sources of error that should be addresses by data quality objectives. Accuracy in laboratory measurements (measurement quality objectives) can be more easily controlled than field sampling variability. Analytical bias needs to be low and precision as high as possible in the laboratory. Sampling variability can be somewhat controlled by strictly following standard procedures and collecting quality control samples, but natural spatial and temporal variability can contribute greatly to the overall error in the parameter value. Resources limit the number of samples that can be taken at one site spatially or over various intervals of time. Finally, laboratory and field errors are further expanded by estimate errors in seasonal loading calculations and modeling estimates.

The Little Spokane River TMDL study poses some significant challenges. The proposed 1998/2004 303(d) list includes parameters that are either quite reactive in the aquatic environment, or they are prone to sample contamination problems. Table 35 summarizes the laboratory accuracy, precision and bias for general water quality measurements and analyses. Due to the large number of analytes, precision and bias for advanced water quality parameters are presented in Appendix D. Stratified seasonal sampling, multiple event sampling, and other sampling design features will be used to better evaluate critical conditions on which to develop TMDL targets for the parameters.

Data quality objectives are more stringent for parameters at sites with fewer samples over the course of the survey than for parameters with larger sample sets. Parameters with relatively large field and laboratory variability (e.g., fecal coliform) will need to have increased numbers of replicate samples in the field and laboratory to increase precision. Some parameters that demonstrate strong diel changes (e.g., D.O. and pH) will need accurate and nearly continuous monitoring during critical seasonal events so rates of change, and diel minimums and/or maximums can be observed. These issues were discussed in the *Sampling Design, Field Procedures, Laboratory Procedures, and Quality Control* sections.

Results of quality control samples summarized in Table 33 will be compared to data quality objectives outlined in Table 35 and Appendix D on a quarterly basis. Data not meeting quality objectives will be qualified and the source(s) of the discrepancies will be investigated and documented. Quality control assessment and documentation will be the responsibility of the project leader responsible for quality assurance as outlined in Section 1 of this document.

Table 35. Summary of the accuracy, precision, and bias of laboratory field and laboratory analysis expressed as a relative standard deviation (RSD)

Analysis	Accuracy % deviation from true value	Precision Relative Standard Deviation	Bias % deviation from true value	Reporting Limits
Field Measurements				
Velocity*	0.1 f/s	0.1 f/s	N/A	0.05 f/s
pH*	0.15 s.u.	0.05 s.u.	0.10 s.u.	1-14 s.u.
Temperature*	0.1^{o}C	0.025 ^{o}C	5	1^{o}C to 40^{o}C
Dissolved Oxygen	15	<5% RSD	5	0.1 mg/L to 15 mg/L
Laboratory Analysis				
Total Suspended Solids	20	<10% RSD	N/A	1 mg/L
Turbidity	20	<10% RSD	N/A	1 NTU
Total Phosphorus	25	<10% RSD	5	10 ug/L
Fecal Coliform	N/A	<25% RSD[2]	N/A	1 cfu/100 mL
Nitrate + Nitrite Nitrogen	25	<10% RSD	5	10 ug/L

8.3 Project Deliverables

In addition to routine progress meetings with Ecology and public information briefings, the completion of this project will result in the following items:

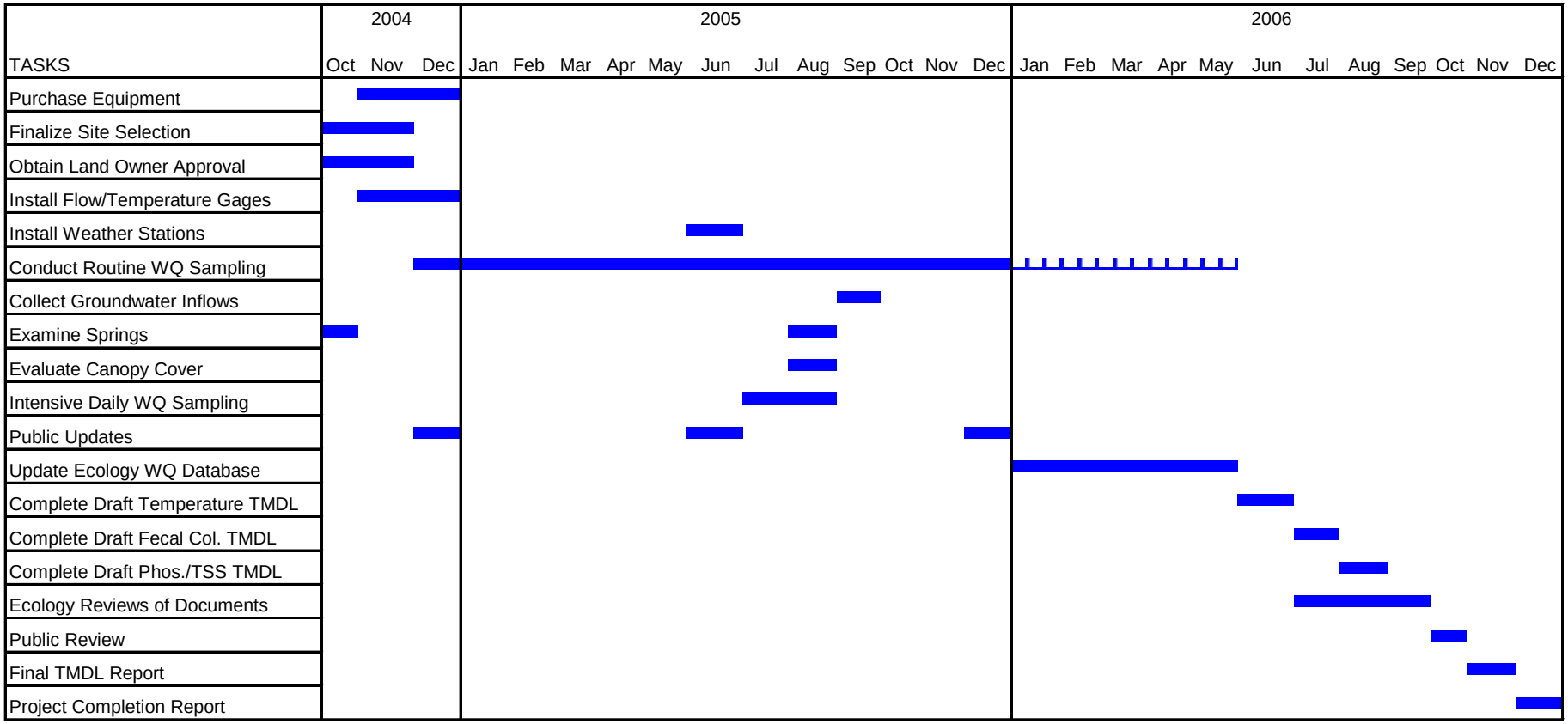
Updated Ecology water quality database,
Monitoring report and assessment,
TMDL modeling and report for temperature,
TMDL modeling and report for fecal coliform bacteria, and
TMDL modeling and report for phosphorus/TSS.

It is anticipated that the phosphorus/TSS TMDL modeling will include the impacts of traditional nutrient/DO cycles. As such, the theoretical impacts of phosphorus and nitrogen species on DO, pH, and algae growth will likely provide extremely valuable information for future assessments. However, given the duration of this proposed project, insufficient time/resources will be spent on developing justifiable DO and pH TMDLs.

8.4 Completion Schedule

The anticipated completion schedule is shown in Table 36.

Table 36. Estimated Completion Schedule for Major Activities



Note: Crosshatched area shown for 'Conduct Routine WQ Sampling' represents schedule yet to be determined; See Section 6.4 for discussion.

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10 APPENDICES

Appendix A. Water quality standards for Washington State

	Washington Code Chapter 173-201A			EPA Criteria
	Class			
	AA	A	Lake	
Temperature	≤ 16°C	≤18°C	NMD[1]	
Dissolved Oxygen (mg/L)	> 9.5	> 8.0	NMD	5.0 mg/L[3]
Fecal Coliform				
Mean (colonies/100mL)	50	100	50	200[4]
< 10% samples exceed	100	200	100	400[4]
pH	6.5 - 8.5	6.5 - 8.5	NMD	
Turbidity				
Background < 50 NTU[2]	< 5 NTU á	< 5 NTU á	< 5 NTU	< 10% reduction in depth of photosynthetic zone[3]
Background > 50 NTU	≤ 10% á	≤ 10% á		
Total Phosphorous				100 µg/L = (0.1 mg/L)[5]
Nitrate	No	State	Standard	10 mg/L[6]
Nitrite	No	State	Standard	1 mg/L[6]

1- No measurable difference from natural conditions
2 - Nephlometric Turbidity Units
3 - Recommended limit for cold water fisheries
4 - Recommended limit for swimming/bathing
5 - Recommended limit to prevent eutrophication
6 - Recommended limit for drinking water supply

* Environmental Protection Agency (EPA) criteria

Appendix B. Water quality data for Little Spokane Watershed from 1998-1999

1998-99 Little Spokane Water Quality Assessment Results

Temperature at point (°C)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	**7.9**	**10.7**	**12.0**	**11.0**	**9.2**	**9.0**	**10.4**	**8.8**	**8.9**	**8.5**
11/2/98	**7.2**	**7.6**	**7.9**	**7.8**	**6.2**	**8.2**	**8.3**	**6.7**	**7.8**	**7.6**
12/7/98	**4.4**	**4.2**	**2.5**	**3.1**	**1.7**	**3.6**	**3.6**	**2.4**	**4.6**	**4.5**
1/11/99	**4.5**	**2.6**	**1.7**	**2.2**	**1.2**	**2.9**	**2.5**	**1.6**	**4.2**	**4.1**
2/8/99	**3.5**	**3.1**	**2.7**	**2.7**	**0.9**	**3.9**	**2.2**	**0.9**	**2.6**	**2.3**
3/8/99	**3.4**	**4.1**	**3.3**	**3.9**	**2.1**	**3.7**	**3.5**	**2.0**	**3.2**	**3.1**
4/5/99	**4.2**	**6.5**	**5.7**	**6.7**	**5.3**	**7.4**	**7.2**	**5.1**	**5.9**	**5.9**
5/3/99	**8.4**	**9.8**	**11.2**	**10.7**	**7.6**	**10.9**	**10.6**	**8.6**	**8.7**	**8.7**
6/7/99	**9.1**	**14.0**	**16.7**	**14.5**	**12.8**	**14.1**	**13.6**	**12.2**	**11.1**	**11.0**
7/12/99	**10.8**	**19.4**	**24.2**	**20.5**	**19.3**	**21.7**	**21.5**	**18.0**	**14.6**	**14.6**
8/9/99	**7.4**	**19.5**	**24.0**	**19.5**	**18.4**	**20.5**	**20.2**	**17.1**	**13.8**	**13.5**
9/13/99	**7.4**	**13.4**	**16.8**	**13.5**	**11.8**	**14.3**	**13.9**	**11.1**	**10.2**	**9.8**

Dissolved Oxygen (mg/L)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	**11.7**	**10.3**	**11.0**	**10.8**	**10.8**	**10.6**	**11.5**	**11.6**	**9.6**	**9.5**
11/2/98	**10.6**	**11.2**	**12.1**	**11.3**	**11.2**	**11.3**	**11.3**	**11.7**	**9.6**	**9.4**
12/7/98		**11.7**	**11.8**	**12.1**	**12.1**	**11.9**	**12.2**	**12.0**	**12.4**	**10.3**
1/11/99	**10.4**	**12.3**	**11.9**	**12.9**	**12.1**		**12.7**	**12.0**	**10.1**	**10.4**
2/8/99		**12.3**	**11.6**	**12.8**	**12.2**	**13.1**	**13.2**	**12.0**	**10.7**	**10.5**
3/8/99	**11.2**	**12.0**	**11.2**	**13.1**	**12.3**	**12.8**	**12.2**	**11.3**	**10.7**	**10.2**
4/5/99	**10.7**	**11.5**	**11.7**	**11.8**	**12.6**	**12.4**	**12.5**	**11.8**	**11.5**	**11.4**
5/3/99	**10.9**	**10.5**	**9.9**	**10.4**	**9.7**	**10.5**	**10.3**	**10.0**	**8.4**	**7.3**
6/7/99	**10.5**	**9.6**	**9.1**	**9.8**	**9.9**	**9.7**	**9.3**	**10.0**	**9.3**	**9.3**
7/12/99	**10.2**	**8.6**	**9.6**	**8.5**	**9.1**	**8.9**	**9.2**	**9.8**	**9.0**	**9.0**
8/9/99	**9.7**	**8.7**	**7.4**	**9.2**	**9.5**	**8.8**	**9.2**	**9.7**	**9.0**	**8.9**
9/13/99	**10.3**	**9.4**	**9.8**	**10.0**	**10.4**	**9.8**	**10.4**	**11.0**	**9.3**	**9.6**

Specific Conductance (µS/cm)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	243	217	120	192	157	264	268	203	221	218
11/2/98	240	219	122	198	181	268	272	258	269	271
12/7/98	207	216	112	151	147	200	207	224	232	236
1/11/99	234	206	93	151	162	202	201	206	240	238
2/8/99	217	199	93	139	103	166	165	117	146	147
3/8/99	221	178	83	112	93	139	142	113	143	142
4/5/99	212	183	78	110	159	138	142	180	221	219
5/3/99	213	193	74	116	119	153	147	143	183	184
6/7/99	224	200	86	142	136	194	180	164	205	206
7/12/99	230	202	90	157	162	215	218	211	248	248
8/9/99	236	206	96	176	186	244	249	230	246	241
9/13/99	234	210	103	184	187	254	259	238	257	253

Numbers in bold for temperature

Date	LS2	LS3	LS4	55B200	LS5	LS6
7/12/99	19.4	24.2	20.5	19.3	21.7	21.5
8/9/99	19.5	24	19.5	18.4	20.5	20.2

Numbers in bold for dissolved oxygen

Date	LS3	55B070
5/3/99	-	7.3
8/9/99	7.4	-

pH

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	8.2	8.2	8.1	8.3	8.3	7.7	8.4	8.3	8.3	8.2
11/2/98	7.5	8.0	8.4	8.3	8.0	8.5	8.5	8.2	8.0	8.0
12/7/98	7.7	8.1	7.1	8.1	8.0	7.8	8.1	7.9	7.8	7.7
1/11/99	7.1	8.0	7.0	7.9	8.0	8.5	8.4	8.2	8.2	8.0
2/8/99	7.8	7.9	7.0	7.5	7.4	7.6	7.6	7.2	7.6	7.3
3/8/99	8.2	[illegible]	7.6	8.4	7.0	[illegible]	8.5	7.5	7.3	7.4
4/5/99	8.1	[illegible]	[illegible]	8.3	7.8	8.4	[illegible]	7.9	8.1	7.8
5/3/99	7.9	8.0	8.0	8.1	7.5	8.2	8.2	7.5	7.5	7.8
6/7/99	8.4	8.5	8.2	8.2	7.9	8.3	8.4	7.9	8.3	8.1
7/5/99	8.2	8.3	[illegible]	8.2	7.9	8.4	8.3	8.3	8.2	8.1
8/2/99	8.1	8.1	7.8	8.1	7.9	8.2	8.3	8.2	8.0	8.2
9/13/99	7.5	7.7	8.2	7.7	8.3	8.3	8.0	8.2	8.2	8.2

* pH meter affected by extreme heat value suspected to be lower

Turbidity (NTU)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	0.7	0.9	1.1	1.0	1.0	1.1	1.0	1.7	1.4	2.2
11/2/98	1.0	0.9	0.7	0.9	1.4	0.9	1.1	1.3	1.3	1.5
12/7/98	1.1	1.3	0.7	1.2	3.3	3.7	3.2	4.6	3.4	4.4
1/11/99	2.0	1.2	1.5	1.7	2.8	3.2	6.9	17.0	17.0	28.0
2/8/99	2.1	1.4	1.6	2.9	5.4	8.5	11.0	17.0	16.0	18.0
3/8/99	1.8	1.4	2.8	3.6	4.3	7.7	13.0	12.0	10.0	9.4
4/5/99	1.2	1.5	2.4	2.2	3.0	4.9	4.9	7.1	5.2	5.1
5/3/99	1.0	1.1	1.1	1.9	4.0	3.2	3.6	6.9	6.2	6.6
6/7/99	1.5	1.1	1.2	2.2	4.5	2.7	3.6	5.0	3.6	4.1
7/12/99	0.8	1.1	1.5	1.5	2.0	1.2	1.7	2.2	1.3	1.7
8/9/99	0.7	0.8	1.0	1.0		0.9	1.2			
9/13/99	0.6	0.5	0.8	0.8		0.6	0.9			

Total Suspended Solids (mg/L)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	<2	<2	<2	2	1	2	2	3	4	6
11/2/98	3	2	<2	2	5	3	3	3	4	6
12/7/98	5	3	<2	4	7	25	8	8	9	9
1/11/99	8	3	<2	3	5	6	16	19	18	24
2/8/99	8	3	<2	6	6	18	31	24	23	24
3/8/99	6	3	<2	7	5	15	46	12	12	9
4/5/99	4	4	<2	4	15	10	8	7	7	8
5/3/99	3	3	3	5	6	8	12	13	15	13
6/7/99	6	3	2	6	8	9	22	13	14	12
7/12/99	2	2	2	4	6	6	7	8	9	8
8/9/99	3	3	<2	3		4	6			
9/13/99	<2	<2	<2	2		2	2			

Numbers in bold for pH

Date	LS2	LS3	LS5	LS6
3/8/99	8.7	-	8.7	-
4/5/99	8.6	8.7	-	8.6
7/5/99	-	9.1	-	-

Total Phosphorus (ug/L)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	17	16	25	15	*10	19	21	15	13	16
11/2/98	19	15	22	20	16	18	19	16	*10	18
12/7/98	27	26	15	25	52	48	45	68	55	52
1/11/99	35	24	22	40	35	48	76	87	63	81
2/8/99	37	23	21	42	52	112	127	106	84	94
3/8/99	33	22	22	36	36	62	103	55	52	52
4/5/99	23	25	22	30	49	53	50	73	61	61
5/3/99	17	19	25	30	46	49	57	60	49	52
6/7/99	26	18	23	31	51	44	55	66	56	55
7/12/99	15	17	22	27	27	30	44	40	27	30
8/9/99	17	18	21	22		32	37			
9/13/99	14	12	16	15		23	24			

Nitrate + Nitrite Nitrogen (mg/L)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	0.14	0.24	0.18	0.38	0.38	1.23	1.15	1.16	1.40	1.37
11/2/98	0.17	0.30	0.14	0.41	0.43	1.31	1.24	1.16	1.29	1.29
12/7/98	0.22	0.44	0.16	0.36	0.37	0.98	0.99	0.95	1.16	1.21
1/11/99	0.23	0.51	0.25	0.48	0.51	1.15	1.07	1.14	1.32	1.28
2/8/99	0.21	0.50	0.21	0.45	0.42	0.87	0.87	0.76	0.94	0.95
3/8/99	0.21	0.50	0.22	0.35	0.27	0.69	0.71	0.63	0.81	0.75
4/5/99	0.19	0.25	0.17	0.21	0.12	0.52	0.50	0.38	0.54	0.52
5/3/99	0.12	0.22	0.10	0.20	0.15	0.50	0.47	0.42	0.66	0.61
6/7/99	0.11	0.20	0.11	0.24	0.22	0.73	0.63	0.59	0.94	0.93
7/12/99	0.09	0.20	0.09	0.25	0.28	0.79	0.71	0.80	1.18	0.28
8/9/99	0.12	0.24	0.12	0.31		1.06	0.95			
9/13/99	0.16	0.26	0.13	0.38		1.19	1.10			

Ammonia Nitrogen (mg/L)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	<0.01	<0.01	0.02	<0.01	*0.01	<0.01	<0.01	*0.01	*0.01	*0.01
11/2/98	0.02	0.01	<0.01	0.01	*0.01	0.01	0.07	*0.01	*0.01	*0.01
12/7/98	0.03	0.11	0.01	0.03	0.04	0.01	<0.01	0.04	0.02	0.04
1/11/99	0.04	0.03	<0.01	0.10	0.07	0.04	0.04	0.04	0.03	0.04
2/8/99	<0.01	<0.01	<0.01	<0.01	0.01	0.04	0.04	0.05	0.04	0.04
3/8/99	<0.01	<0.01	0.01	0.01	*0.01	0.01	0.01	0.02	0.02	0.05
4/5/99	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.03	0.01	0.01
5/3/99	<0.01	0.01	0.01	0.01	0.05	0.03	0.02	0.05	0.05	0.05
6/7/99	0.01	0.01	0.03	0.03	0.02	0.02	0.04	0.02	0.03	0.02
7/12/99	<0.01	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	0.04	0.04	0.04
8/9/99	<0.01	<0.01	0.02	0.01		0.01	0.04			
9/13/99	0.02	0.01	0.01	0.01		0.01	0.01			

* EILS estimated values

Fecal Coliform (Colonies/100ml)

Date	LS1	LS2	LS3	LS4	55B200	LS5	LS6	55B082	55B075	55B070
10/12/98	45	25	34	26	72	23	48	99	36	60
11/2/98	28	22	1	13	10	15	37	63	47	47
12/7/98	59	11	<1	7	5	10	17	9	27	31
1/11/99	48	14	4	80	46	24	80	120	100	52
2/8/99	100	4	3	11	17	60	60	120	48	45
3/8/99	11	<1	1	3	2	6	8	12	11	15
4/5/99	9	11	<1	<1	3	7	6	12	7	5
5/3/99	50	24	6	21	21	30	27	34	37	19
6/7/99	18	16	4	59	23	17	41	25	25	27
7/12/99	54	52	37	43	48	60	99	73	49	49
8/9/99	37	49	34	40		110	110			
9/13/99	5	114	29	18		13	24			

Appendix C. Water quality data for Deadman and Little Deep Creek from 2001-2002

Site Name	River Mile	Discharge (cfs)	Temperature (°C)		pH (units)	Conductivity (µS)
			Air	Water		
Deadman at Fire Station	14.7	2.18	16.1	12.5	6.82	40.9
Deadman at Mt. Spokane Rd.	11.1	2.04	16.4	14.1	7.15	78
Deadman at Bruce Rd.	5.8	1.41	17.4	13.4	7.5	125
Spring above RR	3.6	0.12	20	11.8	8.03	752
Deadman at RR crossing	3.6	1.24	14.8	12.9	7.68	201
Deadman u/s of Kaiser	2.1	2.1	14.9	13	7.67	265
Spring u/s of Kaiser outfall	2	NM	19.3	11.1	7.49	430
Spring u/s of Hwy 2	1.9	NM	17.2	12.1	7.58	601
Deadman at Shady Slope Rd.	0.4	10.1	20.1	11.6	7.8	386
Little Deep S-Fork at Big Meadow	11.5	0.41	15.1	8.4	6.57	50.9
Little Deep N-Fork at Big Meadow	10.4	0.11	14	9.9	6.82	126
Little Deep at Dunn Road	8.3	0.68	13.7	9.2	6.67	102
Little Deep at Woolard Road	6.6	0.31	21.8	9.7	6.85	103
Little Deep at Congleton Prop.	5.4	0.28	16.4	11.2	6.79	107
Little Deep in Colbert	3.7	0.15	20.7	11.4	6.96	108
Little Deep at Hargreaves Prop.	0	1.32	17.2	10.1	7.76	419

Site Name	**DO (mg/l)**	**DO (percent)**	**Nitrate (mg/l)**	**Nitrite (mg/l)**	**TKN (mg/l)**	**Ammonia (mg/l)**
Deadman at Fire Station	7.04	66.2	0.05	0.001	0.08	<0.01
Deadman at Mt. Spokane Rd.	6.26	60.9	0.1	0.001	0.11	0.02
Deadman at Bruce Rd.	5.02	48	0.06	<0.001	0.17	0.04
Spring above RR	7.65	70.4	7.86	0.001	0.06	0.02
Deadman at RR crossing	6.26	59.3	0.81	0.001	0.36	0.03
Deadman u/s of Kaiser	8.76	83.2	0.63	0.001	0.21	0.03
Spring u/s of Kaiser outfall	3.39	30.8	1.8	0.001	0.28	0.04
Spring u/s of Hwy 2	8.29	85.6	3.41	0.001	0.47	0.06
Deadman at Shady Slope Rd.	10.1	92.8	1.01	0.001	0.13	0.01
Little Deep S-Fork at Big Meadow	10.72	91.2	0.08	<0.001	0.31	<0.01
Little Deep N-Fork at Big Meadow	10.83	94.4	0.08	<0.001	0.15	<0.01
Little Deep at Dunn Road	9.97	86.9	0.08	<0.001	0.09	0.01
Little Deep at Woolard Road	10.21	90.3	0.1	0.011	0.1	<0.01
Little Deep at Congleton Prop.	10.61	96.8	0.1	0.001	0.11	<0.01
Little Deep in Colbert	10.77	98.7	0.09	0.001	0.13	<0.01
Little Deep at Hargreaves Prop.	7.45	66.3	0.57	<0.001	0.06	0.01

Appendix D. General field sampling notes provided to each sampling crew describing appropriate collection protocols for various types of samples.

Labeling of Samples
Please include the following information on all sample labels:

1. Site Number
2. Site Name
3. Date
4. Time
5. Team/Group ID (e.g. Group 4)

Field Rinsing Samplers
1. Thoroughly rinse sampler with DI water.
2. Partially fill and rinse the sampler with the water to be sampled.
3. Shake or swirl and then drain the rinse water from the sampler
4. Ensure any nozzles, hoses, bottles, etc. attached to the sampler are rinsed in the same manner.
5. Ensure that as much rinse water as is practical is removed from the sampler prior to collection of field samples (e.g. shake bottles vigorously to remove excess droplets).

Collection of Field Blanks
1. Thoroughly rinse sampler with DI water (same process as field rinse).
2. Fill sampler with DI water so that the DI water enters the sampler in the same manner that a field sample would enter the sampler (e.g. through a nozzle; see example below).
3. Transfer sample to laboratory sample bottles in the same manner that a field sample would be transferred.
4. The following example illustrates the steps for taking a field blank from a DH-48 integrated sediment sampler:

a) Field rinse DH-48 sampler including nozzle and sample bottle.
b) Install rinsed sample bottle in sampler and fill with DI water **through nozzle on sampler** (DO NOT fill sample bottle directly).
c) Remove sample bottle from sampler and deposit sample in field-rinsed composite jug.
d) Reinstall sample bottle in sampler and fill through nozzle on sampler.
e) Repeat steps (c) and (d) until sufficient water exists in composite jug to fill all necessary laboratory sample bottles.
f) Fill laboratory sample bottles from composite jug in the same manner used to transfer other field samples.

Flow Measurement Note:
Pygmy meter – take readings at two depths (.2 and .8) if depth exceeds 1.5 feet
AA meter - take readings at two depths (.2 and .8) if depth exceeds 2.5 feet

Collection of Field Replicate Samples
Field replicates are collected to answer a variety of questions dependent on the study objectives. For the LSR TMDL project, these goals differ across various parameters. Protocols for collection of field replicates is described individually for each parameter or related group of parameters:

General Field Parameter Replicates (Temp, DO, pH)
Goal: Assess variability in field parameters during normal field sampling process (e.g. 1-2 hour site visit).
Method: Sequential sampling

Technique:
1. Conduct all normal field parameter data collection procedures at the outset of site monitoring. Record these values on the principle site data sheet.
2. Conduct all other sampling procedures applicable at the designated site (flow and/or water quality). Record applicable information on the principle site data sheet.
3. Conduct replicate sampling of field parameters (Temp, DO, pH). Record these and other relevant values (sample time, staff gage reading) on a separate data sheet.

Water Quality Replicates
Goal: Assess variability introduced from collection, processing, shipping and lab handling of the samples.
Method: Concurrent sampling

Technique:
1. Complete equipment field-rinsing procedures. Appropriately label 2 sets of sample collection and composite bottles.
2. At the first vertical of an EWI section, collect a sample and pour into a field-rinsed composite bottle.
3. Resample the first vertical and pour into the second composite bottle.
4. Move to second vertical, collect sample, and pour into second composite bottle.
5. Resample second vertical and pour into first composite bottle.
6. Collect and pour sample into each composite bottle in this manner for each of the remaining verticals, alternating composite bottles as described in 2-5 listed above.
7. Process and preserve a sample from the first composite bottle, and a replicate sample from the second composite bottle.
8. Ensure both replicates are recorded on the Chain of Custody form; The first sample is recorded according to site number; The second (replicate) sample is recorded using the designation "D-#" where the number represents the field group number (1-5).

Flow Replicates
Goal: Assess variability in field crew measurement performance (includes variability due to equipment).
Method: Sequential sampling

Technique:

1. Establish stream transect and conduct normal/appropriate flow measurement procedure.
2. Completely remove tape used to establish stream transect.
3. Re-install tape used to establish stream transect.
4. Prepare second flow measurement data sheet with all relevant site information and clearly labeled as “Replicate”
5. Conduct replicate flow measurement procedures using same spacing of verticals as in first stream gauging procedure (e.g. if first flow measurement used 20 verticals spaced 6” apart, the replicate would also use 20 verticals spaced 6” apart).
6. Since the tape marking the transect has been removed and re-established, the relative distance to each vertical may be different between the original and replicate flow measurements.

Appendix E. Information on detection/reporting limits, accuracy, and bias of individual analytes to be determined at the University of Idaho Analytical Sciences Laboratory

University of Idaho Analytical Sciences Laboratory
EPA 507 Analyte List

OP and ON Pesticides

Analyte	EDL (µg/L)
Alachlor	0.050
Ametryn	0.050
Atraton	0.025
Atrazine	0.025
Azinphos methyl	0.050
Benfluralin	0.050
Benthiocarb	0.025
Bromacil	0.050
Butachlor	0.050
Butylate	0.025
Carboxin	0.050
Chlorpyrifos	0.025
Chlorpropham	0.050
Cyanazine	0.025
Cycloate	0.050
Desethyl Atrazine	0.025
2,6-Diethylaniline	0.050
Di-allate	0.050
Diazinon	0.025
Dichlorovos	0.050
Diphenamid	0.050
Disulfoton	0.050
EPTC	0.050
Ethafluralin	0.050
Ethoprop	0.025
Fenamiphos	0.050
Fenarimol	0.050
Fonofos	0.025
Hexazinone	0.050
Malathion	0.050
Metalaxyl	0.050
Metalochlor	0.050
Methidathion	0.050
Methyl Parathion	0.050
Methyl Paraoxon	0.100
Metribuzin	0.025
Mevinphos	0.100
MGK-264	0.050
Molinate	0.025
Napropamide	0.050
Norflurazon	0.050
Pebulate	0.025
Pendimethalin	0.025
Parathion	0.050
Phorate	0.050
Profluralin	0.050
Prometon	0.050
Prometryn	0.025
Pronamide	0.050
Propazine	0.025
Propham	0.050
Simazine	0.025
Simetryn	0.050
Stirofos	0.050
Terbacil	0.050
Terbufos	0.050
Terbutryn	0.050
Tri-allate	0.050
Tricyclazole	0.050
Tridemefon	0.050
Vernolate	0.025

Urea Pests LC/MSD

Analyte	EDL (µg/L)
Deisopropyl atrazine (DIA)	0.025
Diuron	0.025
Fenuron	0.025
Flumeturon	0.025
Linuron	0.050
Monuron	0.025
Neburon	0.025
Siduron	0.025
Tebuthiuron	0.050
Thiodicarb	0.050
Tralkoxydim	0.050

Cl- Acid Herbicides Analyte List

Analyte	EDL µg/L
2,4,6-Trichlorophenol	0.10
2,4,5-Trichlorophenol	0.10
2,3,4,5-Tetrachlorophenol	0.10
2,3,4,6-Tetrachlorophenol	0.10
2,4,5-T	0.08
2,4,5-TP	0.08
2,4-D	0.20
2,4-DB	0.50
2,4-Dichlorobenzoic acid	0.10
3,5-Dichlorobenzoic acid	0.10
Acifluorfen	0.10
Bentazon	0.50
Bromoxynil	0.10
Chloramben	0.09
Dacthal (DCPA)	0.08
Dicamba	0.08
Dichloroprop	0.25
Diclofop methyl	0.25
Dinoseb	0.20
Ioxynil	0.10
MCPA	1.00
MCPP	1.00
Pentachlorophenol	0.08
Picloram	0.15
Triclopyr	0.10

Carbamate Pests LC/MSD

Analyte	EDL µg/L
Aldicarb sulfoxide	0.100
Aldicarb sulfone	0.100
Oxyamyl	0.100
Methomyl	0.100
3-OH Carbofuran	0.100
Aldicarb	0.100
Propoxur	0.100
Carbofuran	0.050
Carbaryl	0.050
Methiocarb	0.050

EPA 507 Extra OP & OC list

Analyze	EDL µg/L
Methamidophos	0.200
Dichlobenil	0.025
Acephate	0.300
Etridiazole	0.025
Chlorneb	0.025
Propachlor	0.025
Trifluralin	0.025
Phorate	0.050
Dimethoate	0.050
Diazinon	0.025
Lindane	0.025
Disulfoton	0.100
Acetachlor	0.025
Methyl Parathion	0.050
Chlorothalonil	0.050
Malathion	0.050
Fenthion	0.050
Trichloronate	0.050
Tetrachlorvinphos	0.050
alpha-Chlordane	0.050
gamma-Chlordane	0.050
Tokuthion	0.100
DEF	0.100
Oxyfluorfen	0.100
Chlorobenzilate	0.050
Fensulfothion	0.100
Methoxychlor	0.025
Phosmet	0.100
cis-permethrin	0.050
Coumaphos	0.050

University of Idaho Analytical Sciences Laboratory

Method Validation Document: EPA Method 507 Detection Limits

Demonstration of Capability of GC/MSD/NPD using the APEX ProSep 800 Large Volume Inlet and NPD detector

Date: 03/21/05
Extraction performed by: KMP\SR
Analysis performed by: TGT

Column Used: DB-XLB 25m x 0.2mm x 0.32µm thickness with 5 m deactivated guard column
Post column flow was split using a Restek MXT 'Y' connector to both the NPD and MSD dectectors
0.7m x 0.1mm restrictor into the MSD and 0.5m x 0.25mm inot the NPD

Representative fortified concentration: 2/5 detection limit in ug/mL
Number of samples: 8

Final extract concentration : 0.04 µg/ml

Dilution factor: 2

T= 2.99800

Analyte	Spike 1 ng/mL	Spike 2 ng/mL	Spike 3 ng/mL	Spike 4 ng/mL	Spike 5 ng/mL	Spike 6 ng/mL	Spike 7 ng/mL	Spike 8 ng/mL	Ave. ng/mL	Rcvry (%)	Expctd (ng/mL)	STD DEV	% RSD	Stat MDL ng/L
Dichlorovos	39.09	31.39	35.35	32.31	31.50	32.63	26.34	31.62	32.53	131.38	24.76	3.64	11	21.8
2,6-Diethylaniline	11.62	12.36	12.49	11.49	13.00	11.78	10.19	12.41	11.92	65.95	18.07	0.86	7	5.2
EPTC	39.96	33.03	34.49	30.73	30.42	30.92	28.86	30.48	32.36	109.81	29.47	3.53	11	21.1
Butylate	31.13	26.73	26.23	23.43	22.04	23.36	17.04	23.83	24.22	68.78	35.22	4.07	17	24.4
Mevinphos	42.66	38.86	37.42	34.80	32.74	34.68	35.06	33.62	36.23	107.41	33.73	3.26	9	19.6
Vernolate	29.32	25.65	25.07	22.66	21.97	22.91	20.15	22.82	23.82	79.82	29.84	2.81	12	16.8
Pebulate	27.25	24.33	23.79	21.91	21.22	21.99	19.80	21.80	22.76	86.28	26.38	2.30	10	13.8
Propham	27.72	24.92	24.43	21.73	21.30	22.36	22.85	21.45	23.35	89.86	25.98	2.22	9	13.3
Molinate	35.22	32.21	30.63	28.28	27.76	28.72	29.80	27.72	30.04	86.83	34.60	2.60	9	15.6
Ethoprop	42.67	39.99	37.54	35.69	33.91	35.88	33.33	34.65	36.71	106.00	34.63	3.21	9	19.3
Cycloate	31.73	29.54	27.95	26.20	25.65	26.39	24.73	25.55	27.22	88.95	30.60	2.37	9	14.2
CIPC	17.93	17.17	16.62	15.91	15.81	16.15	15.64	15.80	16.38	104.86	15.62	0.81	5	4.8
Ethafluralin	21.87	18.65	20.57	17.28	17.29	17.57	13.49	17.15	17.98	70.55	25.49	2.51	14	15.1
Benfluralin	28.35	25.09	26.50	23.05	22.39	22.84	18.81	22.67	23.71	76.91	30.83	2.91	12	17.4
Desethyl Atrazine	31.72	30.01	29.82	30.12	27.96	29.10	29.46	27.67	29.48	105.41	27.97	1.28	4	7.7
Di-allate	29.07	27.99	25.79	23.95	23.26	23.90	19.97	24.04	24.75	84.49	29.29	2.86	12	17.1
Atraton	40.81	38.43	37.42	36.18	33.08	35.80	35.89	34.23	36.48	116.18	31.40	2.42	7	14.5
Simazine	42.66	41.23	39.37	38.24	35.75	38.13	36.43	36.53	38.54	118.16	32.62	2.43	6	14.6
Prometon	46.22	42.88	40.68	39.86	37.23	39.01	36.97	36.68	39.94	124.31	32.13	3.30	8	19.8
Atrazine/Propazine	84.45	81.62	76.71	44.69	70.35	74.37	70.28	70.78	71.66	107.43	66.70	12.11	17	72.6
Profluralin/Terbufos	53.31	50.17	48.86	43.06	42.03	42.20	34.27	40.55	44.31	66.28	66.85	6.12	14	36.7
Pronamide/Fonofos	68.59	67.55	53.29	50.21	48.34	59.58	46.28	50.01	55.48	85.92	64.57	8.72	16	52.3
Diazinon	40.28	38.22	35.75	34.65	32.63	34.92	31.73	32.91	35.14	102.53	34.27	2.91	8	17.5
Disulfoton	10.74	10.25	10.31	9.39	9.60	9.45	8.69	8.78	9.65	35.61	27.10	0.73	8	4.4
Terbacil	45.64	46.60	41.33	40.95	39.22	40.13	36.15	39.54	41.20	128.94	31.95	3.43	8	20.6
Tri-allate	42.17	49.53	36.89	40.79	34.54	39.82	25.95	39.79	38.69	116.00	33.35	6.75	17	40.5
Alachlor	51.08	49.51	44.69	45.16	43.60	44.38	40.46	43.67	45.32	121.53	37.29	3.41	8	20.4
Methyl Paroxen	45.88	45.03	46.77	43.15	39.74	43.02	40.91	43.38	43.49	146.41	29.70	2.39	5	14.3
Metribuzin	27.60	24.07	26.82	23.79	23.48	24.38	26.28	23.21	24.95	92.83	26.88	1.69	7	10.1
Metalaxyl	38.75	41.17	36.35	37.29	35.40	36.52	31.73	34.82	36.50	117.64	31.03	2.79	8	16.7
Simetryn/Ametryn	70.83	66.11	65.45	61.15	57.92	61.96	60.30	57.84	62.70	105.49	59.43	4.48	7	26.9
Methyl parathion	34.02	32.71	34.23	30.93	33.85	37.92	37.63	36.42	34.71	94.18	36.86	2.43	7	14.6
Prometryn/Terbutryn	71.83	69.62	67.43	64.61	59.89	63.61	60.81	61.30	64.89	110.22	58.87	4.36	7	26.2
Bromacil	40.24	38.57	37.63	35.50	33.24	34.98	33.31	33.75	35.90	103.58	34.66	2.63	7	15.8
Malathion	42.85	43.15	40.16	39.56	37.08	39.85	35.59	37.95	39.52	114.53	34.51	2.64	7	15.8
Benthiocarb	47.22	45.73	43.31	41.68	39.98	43.17	37.90	41.93	42.62	109.49	38.92	2.98	7	17.9
Chlorpyrifos	45.02	43.83	42.33	40.81	39.15	40.08	36.49	39.80	40.94	100.09	40.90	2.73	7	16.3
Metalochlor	38.69	37.20	35.81	34.68	33.30	35.89	32.98	32.69	35.16	105.89	33.20	2.14	6	12.8
Cyanazine	38.97	38.05	37.28	35.81	33.46	34.99	33.63	34.68	35.86	108.07	33.18	2.05	6	12.3
Parathion	34.29	32.82	34.11	31.38	30.46	31.40	31.10	30.28	31.98	95.89	33.35	1.57	5	9.4
Tridemefon	44.02	44.92	40.65	40.69	37.75	40.16	35.86	38.99	40.38	125.83	32.09	3.01	7	18.0
MGK-264 (a)/Diphenamid	63.43	60.63	59.26	55.03	50.63	53.85	45.35	54.18	55.30	84.74	65.25	5.79	10	34.7
MGK-264 (b)	45.2	62.56	36.88	46.01	40.82	43.87	25.55	48.67	43.70	131.10	33.33	10.50	24	63.0
Pendimethalin	32.80	30.32	32.91	29.88	29.11	29.91	30.26	28.99	30.52	89.80	33.99	1.52	5	9.1
Methidathion/Tricylcazole	88.29	89.16	82.10	80.14	73.94	78.64	70.43	76.89	79.95	120.77	66.20	6.51	8	39.0
Tetrachlorvinphos	52.65	55.46	51.09	48.97	43.90	47.57	45.79	46.46	48.99	130.53	37.53	3.86	8	23.1
Fenamiphos/Napropamide	36.98	36.92	35.21	32.45	30.69	30.74	26.18	30.21	32.42	51.59	62.85	3.75	12	22.5
Carboxin	5.37	4.72	5.29	4.83	4.68	5.09	4.94	5.43	5.04	53.20	9.48	0.30	6	1.8
Norflurazon	40.65	40.27	38.26	35.88	34.75	30.56	32.45	35.33	36.02	124.12	29.02	3.57	10	21.4
Hexazinone	49.22	49.00	43.76	42.09	39.83	40.48	36.01	41.61	42.75	117.77	36.30	4.52	11	27.1
Azinphos methyl	50.65	54.29	51	47.55	42.47	44.68	40.72	47.18	47.32	155.55	30.42	4.59	10	27.5
Fenarimol	42.87	40.85	38.94	36.83	32.82	33.20	30.15	34.16	36.23	108.01	33.54	4.39	12	26.4

Est'd MDL = Statistical MDL corrected for anlayte recovery.

University of Idaho Analytical Sciences Laboratory
Method Validation Document: EPA Method 507 Detection Limits
Demonstration of Capability of GC/MSD/NPD using the APEX ProSep 800 Large Volume Inlet and MSD detector

Date: 03/21/05
Extraction performed by: KMP\SR
Analysis performed by: TGT

Column Used: DB-XLB 25m x 0.2mm x 0.32µm thickness with 5 m deactivated guard column
Post column flow was split using a Restek MXT 'Y' connector to both the NPD and MSD dectectors
0.7m x 0.1mm restrictor into the MSD and 0.5m x 0.25mm inot the NPD

Representative fortified concentration: 2/5 detection limit in ug/mL
Number of samples: 8

Final extract concentration : 0.04 µg/ml

Dilution factor: 2

T= 2.99800

Analyte	Spike 1 ng/mL	Spike 2 ng/mL	Spike 3 ng/mL	Spike 4 ng/mL	Spike 5 ng/mL	Spike 6 ng/mL	Spike 7 ng/mL	Spike 8 ng/mL	Ave. ng/mL	Rcvry (%)	Expctd (ng/mL)	STD DEV	% RSD	Stat MDL ng/L
Dichlorovos	32.06	28.96	33.67	32.03	32.77	40.19	29.90	39.78	33.67	105.12	32.03	4.18	12	25.1
2,6-Diethylaniline	12.94		12.53	12.13	12.52	12.32	12.46	12.39	12.47	53.73	23.21	0.25	2	1.5
EPTC	35.87	34.36	36.14	34.46	34.62	36.15	29.93	37.26	34.85	99.43	35.05	2.23	6	13.4
Butylate	29.44	28.99	29.37	27.93	26.97	28.85	20.11	30.90	27.82	76.45	36.39	3.32	12	19.9
Mevinphos	48.52	49.68	50.52	49.07	46.38	50.76	48.30	52.55	49.47	123.25	40.14	1.86	4	11.2
Vernolate	34.33	34.13	34.01	32.65	32.08	34.09	27.58	35.33	33.03	89.18	37.03	2.42	7	14.5
Pebulate	32.61	33.57	32.39	31.28	30.87	32.21	26.65	33.64	31.65	84.07	37.65	2.24	7	13.4
Propham	36.18	37.76	36.69	36.09	35.57	36.29	35.20	37.51	36.41	99.40	36.63	0.88	2	5.3
Molinate	36.62	37.18	36.51	35.36	35.05	36.50	35.26	37.47	36.24	94.34	38.42	0.91	3	5.5
Ethoprop	49.16	51.87	50.21	50.05	46.51	52.16	45.78	52.86	49.83	130.36	38.22	2.59	5	15.5
Cycloate	36.69	37.21	36.42	35.67	34.86	36.74	32.73	37.75	36.01	95.79	37.59	1.60	4	9.6
CIPC	40.59	42.81	41.48	41.29	39.83	44.09	39.76	43.45	41.66	114.68	36.33	1.63	4	9.8
Ethafluralin	32.50	32.27	37.23	32.81	31.26	34.19	22.69	36.61	32.45	81.36	39.88	4.47	14	26.8
Benfluralin	27.04	26.31	31.20	27.12	25.94	28.13	19.63	30.11	26.94	82.02	32.84	3.47	13	20.8
Desethyl Atrazine	38.93	40.26	41.83	40.67	36.31	40.19	40.32	42.91	40.18	116.36	34.53	1.96	5	11.8
Di-allate	49.07	41.45	46.21	43.27	39.68	41.71	46.62	42.40	43.80	120.17	36.45	3.18	7	19.0
Atraton	42.36	42.07	44.45	43.81	39.30	44.88	44.58	45.39	43.36	135.74	31.94	2.02	5	12.1
Simazine	39.69	41.21	39.88	41.11	37.11	41.19	37.59	41.19	39.87	145.09	27.48	1.68	4	10.1
Prometon	43.03	43.39	43.98	44.46	39.94	44.88	42.44	44.90	43.38	149.01	29.11	1.64	4	9.9
Atrazine	46.92	47.46	47.32	47.45	43.09	48.58	44.02	48.51	46.67	135.00	34.57	2.02	4	12.1
Propazine	41.55	42.28	41.47	41.85	39.69	42.47	39.19	42.18	41.34	117.73	35.11	1.23	3	7.4
Profluralin	34.30	33.08	39.41	34.90	34.46	36.40	32.94	38.10	35.45	89.63	39.55	2.33	7	14.0
Terbufos	23.96	24.44	24.67	21.78	21.95	21.73	14.49	22.15	21.90	64.51	33.94	3.24	15	19.4
Pronamide	41.54	43.00	42.45	42.63	40.38	43.54	40.34	44.73	42.33	119.43	35.44	1.52	4	9.1
Fonofos	40.54	35.01	41.29	33.32	31.47	41.29	36.59	43.09	37.83	95.52	39.60	4.30	11	25.8
Diazinon	44.57	46.06	44.24	44.91	42.76	46.31	41.32	46.66	44.60	122.03	36.55	1.84	4	11.0
Disulfoton	3.99	3.66	3.96	2.62	2.97	2.77		1.56	3.08	10.15	30.29	0.87	28	5.2
Terbacil	49.00	54.82	52.87	54.82	48.05	52.97	48.77	55.69	52.12	149.82	34.79	3.07	6	18.4
Tri-allate	37.92	39.11	37.22	37.54	35.72	38.01	31.02	39.97	37.06	101.54	36.50	2.75	7	16.5
Methyl Paroxen	65.79	69.53	74.02	72.60	63.94	75.09	71.99	77.12	71.26	163.07	43.70	4.56	6	27.3
Metribuzin	32.36	29.79	37.22	32.03	29.60	33.85	38.07	33.81	33.34	108.57	30.71	3.10	9	18.6
Methyl Parathion	47.13	48.28	52.85	50.92	48.49	52.83	53.58	54.18	51.03	120.67	42.29	2.73	5	16.4
Simetryn	34.57	33.75	35.90	34.27	31.05	35.40	34.74	35.63	34.41	111.44	30.88	1.54	4	9.2
Alachlor	46.03	46.48	46.58	46.54	43.95	47.27	43.76	48.43	46.13	130.79	35.27	1.58	3	9.5
Ametryn	36.95	36.85	37.67	36.74	33.67	37.30	35.42	37.42	36.50	114.03	32.01	1.33	4	8.0
Prometryn	39.39	40.72	41.76	41.08	37.02	41.38	39.28	41.62	40.28	120.82	33.34	1.62	4	9.7
Metalaxyl	48.92	50.16	48.96	49.63	46.00	50.75	45.52	50.38	48.79	146.43	33.32	1.98	4	11.9
Terbutryn	39.39	40.72	41.76	41.08	37.02	41.38	39.28	41.62	40.28	120.82	33.34	1.62	4	9.7
Bromacil	48.66	55.18	52.72	52.63	50.08	52.82	46.62	54.50	51.65	123.63	41.78	2.95	6	17.7
Malathion	46.44	50.44	50.06	50.30	45.22	51.20	47.29	52.66	49.20	136.82	35.96	2.58	5	15.5
Benthiocarb	42.55	43.35	42.72	42.73	40.44	43.80	39.84	44.65	42.51	124.52	34.14	1.62	4	9.7
Chlorpyrifos	39.37	41.25	40.18	40.42	38.06	40.81	35.82	43.23	39.89	113.88	35.03	2.22	6	13.3
Cyanazine	40.91	45.30	44.96	44.27	39.42	44.57	42.46	46.81	43.59	114.22	38.16	2.46	6	14.8
Metalochlor	46.32	47.49	46.77	47.21	44.25	48.78	44.25	48.52	46.70	129.29	36.12	1.72	4	10.3
Tridemefon	47.23	51.57	51.12	52.01	46.99	52.40	47.80	53.02	50.27	144.03	34.90	2.50	5	15.0
MGK-264 (a)	32.72	34.85	31.79	30.60	27.90	30.20	18.00	41.78	30.98	83.32	37.18	6.70	22	40.2
MGK-264 (b)	44.18	46.01	44.54	44.44	41.03	44.55	33.27	48.99	43.38	112.93	38.41	4.64	11	27.8
Diphenamid	41.31	42.25	41.02	41.70	39.38	42.06	38.05	41.93	40.96	117.67	34.81	1.49	4	8.9
Pendimethalin	37.07	37.57	43.98	40.27	38.33	41.86	43.59	42.67	40.67	101.92	39.90	2.75	7	16.5
Methidathion	44.34	49.15	48.33	48.84	43.59	48.89	45.14	51.24	47.44	143.80	32.99	2.72	6	16.3
Tetrachlorvinphos	53.58	60.29	59.08	59.63	53.18	58.97	54.14	62.16	57.63	159.64	36.10	3.46	6	20.8
Butachlor	45.87	48.56	47.70	48.52	44.65	49.12	44.38	49.51	47.29	129.77	36.44	2.04	4	12.2
Fenamiphos	26.79	28.41	31.52	28.00	24.53	26.40	22.95	27.63	27.03	79.87	33.84	2.58	10	15.5
Napropamide	46.24	49.45	47.30	48.54	44.65	48.20	43.16	49.04	47.07	128.02	36.77	2.23	5	13.4

University of Idaho Analytical Sciences Laboratory

Method Detection Limit Study for Oasis Solid Phase Chlorinated Acids Regulated Analytes 2005 using the µECD detector

Date: 03/21/2005
Extraction performed by: SLH 03/15/2005
Analysis performed by: SLH
Detector:µECD

Column Used: DB-XLB 25m x 0.2mm x 0.32µm thickness with 5 m deactivated guard column
Post column flow was split using a Restek MXT 'Y' connector to both the µ-ECD and MSD dectectors
0.7m x 0.1mm restrictor into the MSD and 0.5m x 0.32mm into the µ-ECD

Number of fortified samples: 7 Dilution factor: 8 T= 3.14276

Percent Recovery Data

Analyte	MDL 1	MDL 2	MDL 3	MDL 4	MDL 6	MDL 7	MDL 8	Avg. (ng/mL)	STD Dev.	Average % Rcvry	Rec. (µg/L)	Exp. (ng/mL)	QC check (ng/mL)	% RSD
2,4,6-TCP	24.70	19.92	19.62	22.25	22.54	22.46	25.13	22.37	2.1080	70.09	0.1790	50.00	31.92	9
3,5-DCBA	29.90	21.94	23.93	25.48	23.17	24.63	27.79	25.26	2.7548	85.03	0.2021	50.00	29.71	11
2,4-DCBA	34.03	25.67	27.79	29.32	26.45	28.41	31.10	28.97	2.8638	87.86	0.2317	50.00	32.97	10
2,4,5-TCP	117.33	82.48	88.94	97.14	90.25	98.36	108.21	97.53	11.9738	75.56	0.7802	50.00	129.08	12
Dicamba	38.78	30.82	33.42	33.93	30.18	33.18	36.04	33.76	2.9535	102.75	0.2701	50.00	32.86	9
2,3,4,6-TCP	25.77	19.16	19.48	21.65	20.43	22.46	25.14	22.01	2.6232	75.26	0.1761	50.00	29.25	12
Dichloroprop	41.27	39.55	43.77	37.67	35.47	39.44	38.85	39.43	2.6252	114.76	0.3155	50.00	34.36	7
2,4-D	38.64	38.65	42.16	41.14	37.04	41.85	40.44	39.99	1.9155	98.11	0.3199	50.00	40.76	5
Bromoxynil/2,3,4,5-TCP (CE)	88.78	70.72	74.74	77.08	70.62	79.30	83.77	77.86	6.7081	93.75	0.6229	100.00	83.05	9
Triclopyr	32.87	29.98	32.14	28.95	27.93	31.28	29.52	30.38	1.7821	100.00	0.2431	50.00	30.38	6
Pentachlorophenol	28.77	23.53	23.96	25.22	23.98	26.40	28.19	25.72	2.1228	81.53	0.2058	50.00	31.55	8
2,4,5-TP	37.12	35.43	36.98	35.45	33.22	36.53	36.43	35.88	1.3500	98.57	0.2870	50.00	36.40	4
Chloramben	47.63	53.16	60.96	49.50	51.83	57.32	50.82	53.03	4.6413	114.29	0.4243	50.00	46.40	9
2,4,5-T	41.30	44.09	48.12	41.65	40.37	46.31	40.90	43.25	2.9990	106.52	0.3460	50.00	40.60	7
2,4-DB	59.94	68.28	72.04	64.28	63.23	66.11	59.52	64.77	4.4809	112.61	0.5182	50.00	57.52	7
Dinoseb	93.84	77.83	82.53	84.23	85.24	94.78	97.60	88.01	7.3871	92.44	0.7041	50.00	95.20	8
Bentazon	55.87	44.76	57.92	57.31	47.52	44.37	44.72	50.35	6.3631	152.45	0.4028	50.00	33.03	13
Ioxynil/Picloram (CE)	104.34	98.22	104.65	55.26	100.42	62.77	63.88	84.22	22.3351	82.02	0.6738	100.00	102.68	27
DCPA	55.00	54.34	58.08	54.71	54.17	52.60	33.82	51.82	8.1049	112.33	0.4145	50.00	46.13	16
Acifluorfen	103.51	109.52	112.09	111.47	110.59	110.05	106.31	109.08	3.0795	102.59	0.8726	50.00	106.32	3
Diclofop methyl	37.65	60.93	64.04	57.19	60.75	49.72	46.23	53.79	9.5765	113.12	0.4303	50.00	47.55	18

University of Idaho Analytical Sciences Laboratory

Method Detection Limit Study for Oasis Solid Phase Chlorinated Acids Regulated Analytes 2005 using the MSD detector

Date: 03/21/2005
Extraction performed by: SLH 03/15/2005
Analysis performed by: SLH
Dectector:MSD

Column Used: DB-XLB 25m x 0.2mm x 0.32µm thickness with 5 m deactivated guard column
Post column flow was split using a Restek MXT 'Y' connector to both the µ-ECD and MSD dectectors
0.7m x 0.1mm restrictor into the MSD and 0.5m x 0.32mm into the µ-ECD

Number of fortified samples: 7 Dilution factor: 8 T= 3.14276

Percent Recovery Data

Analyte	MDL 1	MDL 2	MDL 3	MDL 4	MDL 6	MDL 7	MDL 8	Avg. (ng/mL)	STD Dev.	Average % Rcvry	Rec. (µg/L)	Exp. (ng/mL)	QC check (ng/mL)	% RSD
2,4,6-TCP	25.63	21.81	21.14	23.76	23.54	23.67	26.26	23.69	1.8454	73.61	0.1895	50.00	32.18	8
3,5-DCBA	30.19	23.25	23.72	25.66	24.52	25.85	28.15	25.91	2.4902	89.02	0.2072	50.00	29.10	10
2,4-DCBA	35.04	27.72	28.99	30.14	28.08	29.21	32.13	30.19	2.5898	94.60	0.2415	50.00	31.91	9
2,4,5-TCP	95.37	66.43	69.44	76.84	73.18	77.78	88.91	78.28	10.4241	79.85	0.6262	50.00	98.03	13
Dicamba	37.25	28.88	31.92	32.42	29.20	31.12	34.30	32.16	2.9216	98.28	0.2572	50.00	32.72	9
2,3,4,6-TCP	27.69	21.12	21.55	24.14	23.19	24.72	27.11	24.22	2.5314	80.94	0.1937	50.00	29.92	10
MCPP	37.83	31.42	34.63	34.62	30.80	33.29	35.17	33.97	2.3879	97.63	0.2717	50.00	34.79	7
MCPA	42.93	35.64	36.85	37.98	34.38	35.02	37.11	37.13	2.8483	100.13	0.2970	50.00	37.08	8
Dichloroprop	38.34	33.92	35.54	35.71	32.11	33.42	36.53	35.08	2.0921	101.45	0.2807	50.00	34.58	6
2,4-D	47.51	38.46	44.63	43.41	41.56	41.50	43.08	42.88	2.8285	114.80	0.3430	50.00	37.35	7
Bromoxynil	39.44	30.93	34.13	34.87	31.13	34.38	36.56	34.49	2.9731	104.46	0.2759	50.00	33.02	9
2,3,4,5-TCP	49.69	40.97	42.46	44.08	41.10	43.24	45.28	43.83	3.0100	92.28	0.3507	50.00	47.50	7
Triclopyr	41.63	37.03	37.66	39.70	35.99	37.08	37.78	38.12	1.9127	107.45	0.3050	50.00	35.48	5
Pentachlorophenol	30.63	25.80	25.51	27.37	26.87	27.46	29.89	27.65	1.9418	89.33	0.2212	50.00	30.95	7
2,4,5-TP	38.30	38.48	37.90	36.43	36.61	36.77	35.19	37.10	1.1854	115.89	0.2968	50.00	32.01	3
Chloramben	51.43	55.49	57.05	55.15	53.39	51.43	50.22	53.45	2.5367	121.87	0.4276	50.00	43.86	5
2,4,5-T	44.07	42.40	47.30	43.23	41.00	41.78	42.12	43.13	2.0895	112.26	0.3450	50.00	38.42	5
2,4-DB	51.72	52.33	53.19	52.43	49.13	47.77	47.28	50.55	2.4317	104.66	0.4044	50.00	48.30	5
Dinoseb	99.91	83.87	84.49	87.96	87.61	94.68	96.23	90.68	6.2385	97.41	0.7254	50.00	93.09	7
Bentazon	44.09	43.36	45.00	44.47	41.96	41.33	41.72	43.13	1.4642	111.77	0.3451	50.00	38.59	3
Ioxynil	50.06	42.74	44.46	45.43	44.01	46.03	45.88	45.52	2.3145	99.86	0.3641	50.00	45.58	5
Picloram	58.81	60.07	61.52	60.91	57.24	54.27	54.76	58.23	2.8992	120.33	0.4658	50.00	48.39	5
DCPA	53.90	55.28	58.15	57.99	54.66	51.55	35.87	52.49	7.6798	120.49	0.4199	50.00	43.56	15
Acifluorfen	109.46	113.17	111.95	106.46	109.46	101.97	102.43	107.84	4.4004	110.42	0.8627	50.00	97.67	4
Diclofop methyl	50.91	50.22	49.18	48.45	45.84	41.96	42.73	47.04	3.5935	109.50	0.3763	50.00	42.96	8

Note: Acifluorfen shows enhancement on the MSD

University of Idaho Analytical Sciences Laboratory

Method Validation Document: EPA Method 507 Modified Detection Limits for ISDA GW Monitoring Analytes Continuous Liquid/Liquid
Demonstration of Capability: Liquid/Liquid Extraction follwed by Large Volume GC/MSD using the APEX ProSep 800 Inlet and MSD detector

Date: 03/26/04 — Column Used: DB-XLB 25m x 0.2mm x 0.3um thickness
Extraction performed by: TGT — Extraction: 1 liter of water extracted and concentrated to 2 mL
Analysis performed by: TGT

Representative fortified concentration: 2 to 5 times detection limit — Final extract concentration : 0.025 µg/ml — Dilution factor: 2
Number of samples: 8 — Equivalent to 0.05 µg/L — T= 2.99800

Analyze	Spike 1 ng/mL	Spike 2 ng/mL	Spike 3 ng/mL	Spike 4 ng/mL	Spike 5 ng/mL	Spike 6 ng/mL	Spike 7 ng/mL	Spike 8 ng/mL	Ave. ng/mL	Rcvry (%)	Expctd (ng/mL)	STD DEV	% RSD	Stat MDL ng/L
Methamidophos	73.50	67.02	62.33	54.66	29.67	78.84	54.08	53.22	59.17	**35.91**	164.77	15.19	26	91.1
Dichlorovos	27.12	27.59	28.26	26.78	25.56	27.73	25.13	25.59	26.72	**90.39**	29.56	1.16	4	7.0
Dichlobenil	21.10	21.51	22.45	21.22	22.57	23.06	21.26	22.76	21.99	**86.41**	25.45	0.80	4	4.8
Mevinphos	37.45	37.97	39.45	36.16	32.80	35.73	31.92	31.45	35.37	**90.73**	38.98	2.98	8	17.9
Acephate	101.77	90.88	215.62	141.03	20.78	117.31	98.65	35.69	102.72	**30.05**	341.82	60.70	59	364.0
Etridiazole	36.59	36.06	37.29	35.23	33.28	36.16	33.68	33.30	35.20	**86.33**	40.77	1.58	5	9.5
Chlorneb	21.85	22.00	22.35	21.87	22.66	23.39	20.93	22.42	22.18	**84.00**	26.41	0.72	3	4.3
Captan	7.40	5.20	5.85	6.31	5.93	9.03	7.68	7.02	6.80	**104.17**	6.53	1.23	18	7.4
Propachlor	27.60	28.16	29.05	27.72	27.44	27.29	25.43	27.02	27.46	**90.94**	30.20	1.03	4	6.2
Ethoprop	27.91	29.99	28.56	28.42	27.78	28.83	25.45	26.89	27.98	**91.55**	30.56	1.36	5	8.1
Trifluralin	28.10	29.60	30.35	29.00	27.27	28.98	26.18	26.54	28.25	**89.38**	31.61	1.49	5	8.9
Naled	81.65	96.27	101.25	83.82	38.77	66.92	63.07	49.65	72.68	**100.53**	72.29	21.98	30	131.8
Phorate	24.70	25.02	25.53	18.42	22.22	24.28	21.88	21.64	22.96	**79.98**	28.71	2.38	10	14.3
Dimethoate	44.29	45.68	47.50	43.25	33.52	37.89	34.25	31.64	39.75	**88.01**	45.17	6.17	16	37.0
Diazinon	29.42	30.35	30.41	29.48	27.99	29.99	28.33	28.61	29.32	**91.21**	32.15	0.92	3	5.5
Lindane	24.31	24.08	24.62	23.16	23.21	24.70	22.26	23.92	23.78	**86.23**	27.58	0.84	4	5.0
Disulfoton	17.15	17.59	16.72	10.78	13.21	15.58	14.62	12.90	14.82	**78.24**	18.94	2.39	16	14.3
Acetachlor	28.90	30.30	29.82	29.11	27.61	28.07	25.97	27.73	28.44	**88.35**	32.19	1.39	5	8.3
Methyl Parathion	36.98	38.84	40.76	36.17	28.59	30.29	27.03	26.86	33.19	**80.30**	41.33	5.61	17	33.6
Chlorothalonil	31.30	32.30	33.66	31.59	27.92	29.38	27.28	27.26	30.09	**94.11**	31.97	2.46	8	14.8
Malathion	40.09	40.09	41.74	39.78	33.49	36.83	34.74	33.43	37.52	**92.04**	40.77	3.32	9	19.9
DCPA (parent)	23.90	24.56	24.82	23.42	24.42	24.18	23.02	24.38	24.09	**90.05**	26.75	0.61	3	3.6
Chlorpyrifos	30.82	30.00	31.41	29.37	28.30	28.47	26.95	27.54	29.11	**87.91**	33.11	1.57	5	9.4
Fenthion	24.43	25.24	26.22	18.88	21.96	23.68	21.58	21.57	22.95	**81.54**	28.14	2.39	10	14.3
Trichloronate	27.57	27.40	28.98	27.74	26.69	27.26	25.23	25.47	27.04	**89.25**	30.30	1.23	5	7.4
Methidathion	40.71	43.69	46.78	39.13	31.27	32.96	30.42	29.08	36.76	**85.32**	43.08	6.69	18	40.1
Tetrachlorvinphos	57.18	58.06	62.73	54.56	37.25	41.99	36.22	34.30	47.79	**87.23**	54.78	11.48	24	68.9
alpha-Chlordane	23.24	23.78	24.87	23.42	24.04	24.33	23.13	24.07	23.86	**89.03**	26.80	0.59	2	3.5
gamma-Chlordane	23.99	24.64	24.94	23.99	24.38	24.44	22.87	24.57	24.23	**90.00**	26.92	0.63	3	3.8
Fenamiphos	37.42	37.81	40.33	34.62	25.89	27.77	24.53	23.37	31.47	**78.06**	40.31	6.79	22	40.7
DEF	42.21	40.97	46.61	37.99	29.05	39.21	32.53	31.33	37.49	**74.47**	50.34	6.03	16	36.2
Oxyfluorfen	36.99	36.71	39.07	35.82	29.71	30.35	29.62	28.66	33.37	**89.43**	37.31	4.17	12	25.0
Chlorobenzilate	31.51	32.59	36.59	33.91	27.70	29.68	26.72	25.05	30.47	**91.28**	33.38	3.90	13	23.4
Fensulfothion	51.97	53.27	57.72	56.43	38.48	40.23	36.41	33.25	45.97	**86.39**	53.21	9.85	21	59.1
Methoxychlor	45.49	46.22	47.14	45.14	39.43	38.90	36.85	27.99	40.90	**87.46**	46.76	6.50	16	39.0
Phosmet	55.56	56.89	64.71	57.72	24.08	37.81	33.75	30.13	45.08	**89.27**	50.50	15.31	34	91.8
Azinphos methyl	149.88	154.47	165.70	154.76	100.96	105.30	95.15	90.77	127.12	**85.47**	148.73	31.67	25	189.9
cis-permethrin	36.01	37.16	38.48	36.49	34.58	31.29	28.68	30.80	34.19	**90.78**	37.66	3.51	10	21.0
Coumaphos	60.61	63.53	70.35	61.55	43.99	42.02	38.67	37.78	52.31	**82.81**	63.17	12.97	25	77.8