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Quality Assurance Project Plan

Assessment of Aquatic Toxicity in North Creek, Gig Harbor

November 2009

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Author and Contact Information

Brandee Era-Miller
P.O. Box 47600
Environmental Assessment Program
Washington State Department of Ecology
Olympia, WA 98504-7710

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

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

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

Quality Assurance Project Plan

Assessment of Aquatic Toxicity in North Creek, Gig Harbor

November 2009

Approved by:

Signature: Date: November 2009
Sally Lawrence, Client, Water Quality Program, NWRO

Signature: Date: November 2009
Dave Garland, Client's Unit Supervisor, Water Quality Program, NWRO

Signature: Date: November 2009
Kevin Fitzpatrick, Client's Section Manager, Water Quality Program, NWRO

Signature: Date: November 2009
Brandee Era-Miller, Author / Project Manager / EIM Data Engineer, EAP

Signature: Date: November 2009
Scott Collyard, Directed Studies Unit, EAP

Signature: Date: November 2009
Dale Norton, Author's Unit Supervisor, Toxics Studies Unit, EAP

Signature: Date: November 2009
Will Kendra, Author's Section Manager, EAP

Signature: Date: November 2009
Robert F. Cusimano, Section Manager for Project Study Area, EAP

Signature: Date: November 2009
Stuart Magoon, Director, Manchester Environmental Laboratory, EAP

Signature: Date: November 2009
Bill Kammin, Ecology Quality Assurance Officer

Signatures are not available on the Internet version.
NWRO - Northwest Regional Office
EAP - Environmental Assessment Program
EIM - Environmental Information Management system

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Abstract

North Creek is listed on the 2006 federal Clean Water Act Section 303(d) list for elevated concentrations of lead and copper. In 2008, the Washington State Department of Ecology (Ecology) conducted a study on North Creek that verified elevated concentrations of lead and copper.

The Gig Harbor Sportsman's Club has been identified as the likely source of lead to North Creek based on sampling efforts by the Tacoma-Pierce County Health Department in 2002 and by Ecology in 2008.

This study will assess for potential adverse biological effects in North Creek due to elevated levels of lead and copper. Bioassay tests (daphnid and trout) and periphyton will be used to evaluate aquatic toxicity. Total and dissolved concentrations of lead and copper will also be measured in surface waters.

Each study conducted by Ecology must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Background

North Creek drains a watershed of approximately 0.2 square miles (130 acres) made up of mixed forest, family residences, a shooting range, athletic fields, and a business park. North Creek is within Water Resource Inventory Area (WRIA) 15. The creek flows north to south and discharges to Donkey Creek, a salmon-bearing stream which flows through the city of Gig Harbor and into Puget Sound (Golding, 2008).

North Creek is listed on the 2006 federal Clean Water Act Section 303(d) list for elevated concentrations of lead and copper in surface water.

The Gig Harbor Sportsman's Club has been identified as the likely source of lead to North Creek based on sampling efforts by the Tacoma-Pierce County Health Department (TPCHD) in 2002 and the Washington State Department of Ecology (Ecology) in 2008.

The TPCHD, in conjunction with Ecology's Toxics Clean-up Program, recently completed a site hazard assessment for Gig Harbor Sportsman's Club. The site received a high priority ranking of 1 and is currently awaiting future clean-up action by Ecology (Matthews, 2009.)

North Creek flows across the Gig Harbor Sportsman's Club property. The headwaters of the creek are within one mile of the club. The club is an active shooting range located off Burnham Drive in Gig Harbor. It has operated since the 1940s. Club property consists of a shotgun range with seven regulation trap fields as well as a rifle and pistol range (Golding, 2008).

In the spring of 2008, sampling conducted by Ecology showed that lead concentrations below the Sportsman's Club property were the highest concentrations of lead found in the waters of Washington State (Golding, 2008). Table 1 shows how dissolved lead concentrations below the Sportsman's Club property boundary increase by three orders of magnitude compared to levels just above the club property boundary. Washington State water quality criteria for dissolved lead were also grossly exceeded below the club property boundary.

Table 1. Lead Concentrations in North Creek Above and Below the Sportsman's Club.

Station	Lead – TR (ug/L)	Lead – Diss (ug/L)	Hardness (mg/L)	Water Quality Criteria*	
				Acute	Chronic
Collected 4/10/2008					
N Creek Above	1.15	**0.82**	12.5	6.33	0.25
N Creek Below	212	**200**	11.1	5.53	0.22
Collected 4/21/2008					
N Creek Above	1.44	**0.82**	13	6.62	0.26
N Creek Below	188	**178**	10	4.91	0.19

* Water quality criteria are for dissolved lead and are based on hardness (WAC 173-201A).
TR = total recoverable.
Diss = dissolved.
Bold = levels exceed (do not meet) water quality criteria.

Ecology also analyzed copper (Table 2). Copper concentrations exceeded criteria, but not by much. Copper was slightly lower in North Creek below the Sportsman's Club as compared to the site above the Sportsman's Club, indicating that the Sportsman's Club is not a major source of copper to the creek.

Table 2. Copper Concentrations in North Creek Above and Below the Sportsman's Club.

Station	Copper – TR (ug/L)	Copper – Diss (ug/L)	Hardness (mg/L)	Water Quality Criteria*	
				Acute	Chronic
Collected 4/10/2008					
N Creek Above	2.71	**2.19**	12.5	2.40	1.92
N Creek Below	2.30	**1.96**	11.1	2.14	1.73
Collected 4/21/2008					
N Creek Above	2.68	**2.41**	13	2.49	1.99
N Creek Below	2.6	**2.08**	10	1.94	1.59

* Water quality criteria are for dissolved copper and are based on hardness (WAC 173-201A).
TR = total recoverable.
Diss = dissolved.
Bold = levels exceed water quality criteria.

The 2008 Ecology study (Golding, 2008) recommended bioassessment of North Creek below the Club boundary to determine if adverse impacts are occurring due to high lead concentrations. The current study will assess the potential for adverse biological impacts to North Creek.

Project Description

The main objective for the project will be to assess the potential for adverse biological impacts in North Creek from elevated levels of lead and copper. Samples will be taken from North Creek both directly above and below the Sportsman's Club property.

Biological impacts will be assessed using aquatic toxicity laboratory bioassays and in-situ periphyton. Water samples will also be analyzed for total and dissolved lead and copper.

Results from the current project, along with the recent Site Hazard Assessment ranking of the Sportsman's Club property, may be used to support future clean-up action by Ecology's Toxics Cleanup Program.

Organization and Schedule

The following people are involved in the North Creek Study. All are employees of the Washington State Department of Ecology.

Table 3. Organization of Project Staff and Responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Sally Lawrence Water Quality Program Northwest Regional Office Phone: (425) 649-7036	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
Brandee Era-Miller Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6771	Project Manager/ Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Tanya Roberts Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-7392	Field Assistant	Helps collect samples and records field information.
Scott Collyard Directed Studies Unit Western Operations Section Phone: (360) 407-6455	Lead for Periphyton Collection	Leads collection and analysis of periphyton samples and provides final data to project manager.
Dale Norton Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

EAP – Environmental Assessment Program.
EIM – Environmental Information Management system.
QAPP – Quality Assurance Project Plan.

Table 4. Proposed Schedule for Completing Field and Laboratory Work, Data Entry into EIM, and Technical Reports.

Field and laboratory work	Due date	Lead staff
Field work completed	December 2009	Brandee Era-Miller
Laboratory analyses completed	April 2010	
Environmental Information System (EIM) database		
EIM user study ID	BERA0007	
Product	Due date	Lead staff
EIM data loaded	May 2010	Brandee Era-Miller
EIM quality assurance	June 2010	Tanya Roberts
EIM complete	July 2010	Tanya Roberts
Final report		
Author lead	Brandee Era-Miller	
Schedule		
Draft due to supervisor	May 2010	
Draft due to client/peer reviewer	June 2010	
Draft due to external reviewer(s)	July 2010	
Final (all reviews done) due to publications coordinator	August 2010	
Final report due on web	September 2010	

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that the data can be used to (1) evaluate aquatic toxicity in North Creek and (2) determine if elevated lead and copper levels may be the primary cause of toxicity. These objectives will be achieved by following the *Sampling Procedures* and *Quality Control Procedures* described in this Quality Assurance Project plan.

Metals, Hardness, and Total Suspended Solids

Ecology's Manchester Environmental Laboratory (MEL) will perform chemical analysis for metals, hardness, and total suspended solids (TSS). The analytical measurement quality objectives (MQOs) for the project are shown in Table 5. MQOs for laboratory control samples, laboratory duplicates, matrix spikes, and matrix spike duplicates are MEL's acceptance limits for the selected analyses.

Table 5. Analytical Measurement Quality Objectives for Metals, Hardness, and TSS.

Analyte	Laboratory Control Samples	Laboratory Duplicates	Matrix Spikes	Matrix Spike Duplicates	Required Reporting Limits*
	% recovery limits	RPD (%)	% recovery limits	RPD (%)	
Lead	85 – 115	20	75 - 125	20	0.02 ug/L
Copper	85 – 115	20	75 - 125	20	0.16 ug/L
Hardness	85 – 115	20	75 - 125	20	1 mg/L
TSS	80 – 120	20	N/A	N/A	1 mg/L

* = for dissolved metals only.
N/A = not applicable.
RPD = relative percent difference.

The required reporting limits for the project are the reporting limits that MEL must meet to serve the objectives of the project. For hardness and TSS, MEL's routine reporting limits are used. For lead and copper, the required reporting limits are based on Washington State water quality criteria which are dependent on hardness. Hardness values from the 2008 Ecology study on North Creek ranged from 10 – 13 mg/L (Golding, 2008). The water quality criteria for dissolved lead and copper are given in Table 6. The required reporting limits are a factor of 1/10 of the criteria.

Table 6. Applicable Freshwater Criteria for Dissolved Metals (ug/L)* for the Protection of Aquatic Life (WAC 173-201A).

Metal	Acute	Chronic
Lead	4.91	0.2
Copper	1.94	1.6

* based on a hardness of 10 mg/L.

Field Measurements

A Hydrolab MiniSonde® meter will be used to measure water temperature, pH, conductivity, and dissolved oxygen onsite. Calibration of the MiniSonde® meter before and after field sampling will be sufficient to ensure measurements are accurate. One Winkler dissolved oxygen sample will also be collected per sampling event to check the accuracy of the dissolved oxygen results from the MiniSonde®.

Toxicity Bioassays

Toxicity bioassays will be performed by Nautilus Environmental. They are an accredited laboratory for the selected bioassay tests. They are expected to meet the quality control requirements of the bioassay methods used for the project.

Periphyton

Periphyton will be collected under the supervision of Scott Collyard of Ecology's Environmental Assessment Program (EAP). He is specialized in periphyton collection. Periphyton will be collected by carefully following standard protocols. The contract laboratory will be an accredited laboratory for periphyton analysis.

Sampling Process Design (Experimental Design)

To assess for potential adverse biological impacts to North Creek from elevated levels of lead and copper, samples will be taken both directly above and below the Sportsman's Club property on North Creek. The sampling locations coincide with sites NCREEK1 and NCREEK2 from Ecology's 2008 North Creek study (see Figure 1).

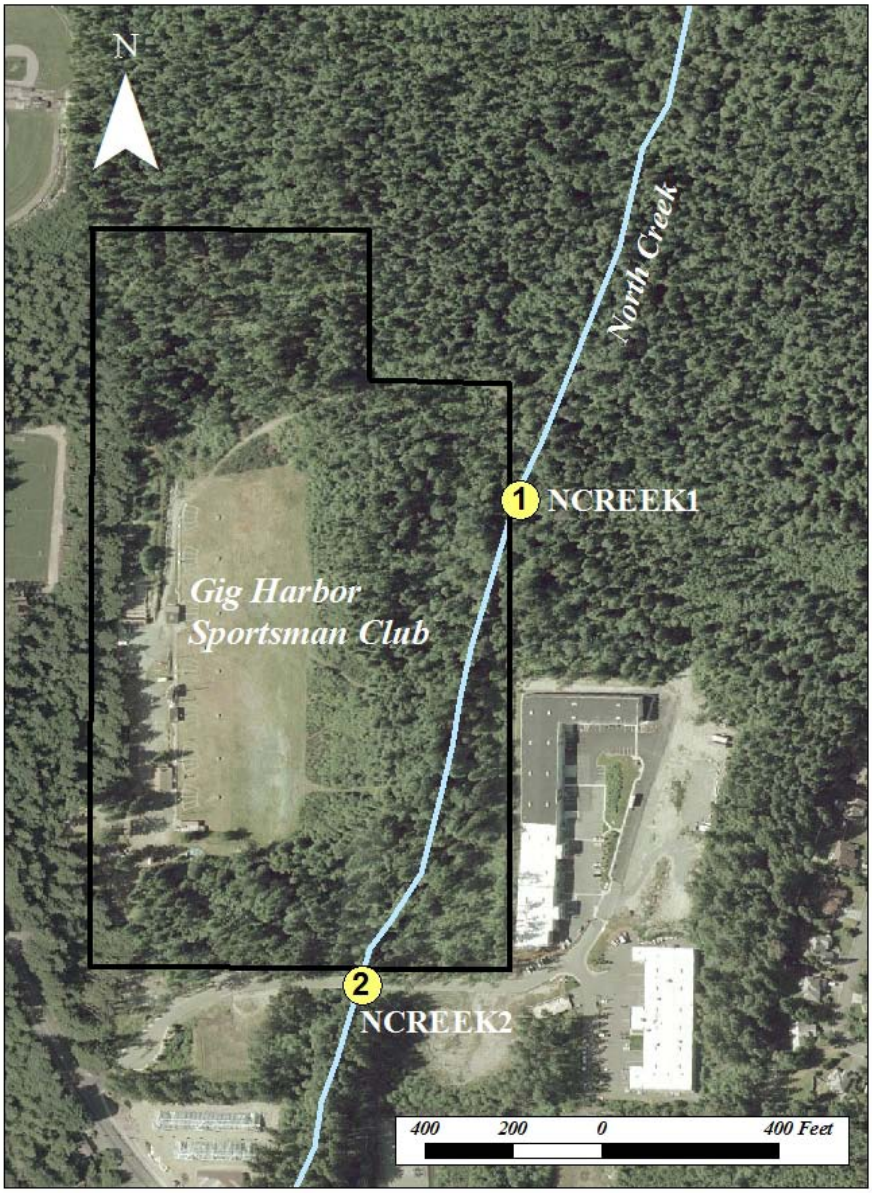

Figure 1. North Creek Sampling Locations.

Biological effects will be measured using aquatic toxicity bioassays and periphyton. Both an acute test (48-hour daphnid survival) and a chronic test (7-day trout survival and growth) will be used. Both tests are known to be sensitive to metals (Rempel-Hester, 2009).

Water samples for metals analysis will be collected at the same time as water for the bioassay tests is collected. Periphyton will be collected from the creek substrate within a few hours of collection of water samples for bioassays and metals analyses.

The target window for sample collection will be November through December 2009 to ensure adequate flow since North Creek is an intermittent creek. Average rainfall for the Tacoma-Narrows Airport indicates that November is the 3rd wettest month for the area with a monthly average of 5.75 inches. December and January are the other wettest months at 6.01 and 5.76 inches, respectively.

Bioassays and water chemistry samples will be collected twice, between 1-4 weeks apart depending on rainfall and adequate streamflow. Periphyton will be collected on only one of the sampling dates, preferably after several weeks of continuous flow in the creek. Continuous flow will allow for periphyton communities to become established in the creek (Collyard, 2009). See Table 7 for the sampling schedule.

Table 7. Field Sampling Schedule for the North Creek Toxicity Study.

Analysis	Number of Sample Locations, November-December 2009	
	Sample Date #1	Sample Date #2
Periphyton	--	2
Acute bioassay (48-hr Daphnid)	2	2
Chronic bioassay (7-day Trout)	2	2
Metals, TSS, and hardness	2	2
Temperature, conductivity, dissolved oxygen, and pH	2	2

Ancillary laboratory parameters will also be analyzed and include hardness and TSS. Field measurements will include water temperature, conductivity, dissolved oxygen, and pH. These additional parameters will help to provide a more complete picture of water quality conditions at each site.

Dissolved metals are more important for the current study than total metals because Washington State water quality standards only apply to dissolved metals (WAC 173-201A). The dissolved fraction is also what is typically considered available to aquatic organisms. Measuring both the dissolved and total fractions gives a ratio of how much of a metal is bio-available in the water column and how much is tied up in the particulate form.

Sampling Procedures

Water Samples

All water samples will be collected by hand as simple grabs from mid-channel following the EAP *Standard Operating Procedure (SOP) for Grab sampling – Fresh water, Version 1.0* (Joy, 2006). Streamflow in North Creek is small and well-mixed so that single grabs will be adequate to represent creek water. Powder-free nitrile gloves will be worn by field staff when collecting and handling samples.

After collection, samples will be labeled, put on ice in coolers, and kept cool at 4° C. Chain-of-custody will be maintained. Samples will be delivered to the laboratories within the allowable holding times for each analysis. Containers, preservations, and holding times are shown in Table 8.

Table 8. Recommended Containers, Preservations, and Holding Times.[1]

Analyte	Container	Preservation	Holding Time
Metals in Water[1]			
Lead and copper - TR	1 liter pre-cleaned HDPE bottle	HNO_3 to pH<2	6 months
Lead and copper - Diss	1 liter pre-cleaned HDPE bottle	HNO_3 to pH<2	6 months
Hardness	Pre-acidified 125 mL bottle	H_2SO_4 to pH<2	6 months
Total suspended solids	1 liter wide-mouth polyethylene bottle	Refrigerate or ice, cool to 4° C	7 days
Water Toxicity Bioassays[2]			
48-hr Daphnid	3 of the 10-liter LDPE cubitainers (30 liters total) will cover both tests	Refrigerate or ice, cool to 6° C	36 hours
7-day Trout		Refrigerate or ice, cool to 6° C	36 hours

[1] = Information taken from the Manchester Laboratory Users Manual (MEL, 2008).
[2] = Personal communication with Nautilus Environmental Laboratory.
TR = total recoverable.
Diss = dissolved.

Metals

Collection of water samples for metals analysis will follow the EAP *Standard Operating Procedure (SOP) for the Collection and Field Processing of Metals Samples, Version 1.3* (Ward, 2007). Dissolved metals will be filtered in the field using 0.45 micron pre-cleaned Nalgene filters. Samples will be preserved in the field using 1:1 nitric acid from small Teflon® vials. Filtering and preservation will be conducted on a clean lab table in the field van using clean methods. Samples will be filtered and preserved within 15 minutes of collection.

Toxicity Bioassays

Water for bioassays will be collected in cubitainers provided by the testing laboratory. Holding time is critical for bioassays. Samples will be taken directly to Nautilus Environmental in Fife, Washington, on the day of collection.

Field Measurements

A Hydrolab MiniSonde® meter will be used to measure water temperature, pH, conductivity, and dissolved oxygen onsite. One Winkler dissolved oxygen sample will be collected per sampling event to check the accuracy of the dissolved oxygen results from the MiniSonde®. The MiniSonde® meter will be calibrated before and after field sampling following the instruction manual for the meter.

Flow will be measured using a Marsh McBirney flow meter and top-setting rod or by other methods as described in the EAP *SOP for Estimating Streamflow, Version 1.0* (Sullivan, 2007).

Periphyton

Periphyton will be collected under the supervision of Scott Collyard who is specialized in periphyton collection. Ecology's periphyton collection method is a modification of methods described in Wyoming's *Manual of Standard Operating Procedures for Sample Collection and Analysis* (WDEQ, 2005). Ecology's draft periphyton collection method is included in Appendix B.

A general description of periphyton collection includes collecting rocks (2.5 – 4" in diameter) or woody debris (0.5 – 2" in diameter and 3 – 5" in length) from 8 quadrants across a riffle in the stream. The periphyton on the rocks or wood is then gently scrubbed and rinsed off into a container. The rinsate is poured into a 500 mL Nalgene sample bottle and preserved. Samples are kept in a darkened cooler and sent to a laboratory for analysis.

Foil templates of the rocks or wood are taken to match the areas where the periphyton were attached. The templates are later used to calculate the total area of periphyton collection.

Measurement Procedures

Metals, hardness, and TSS analyses will be conducted by Ecology's MEL located in Manchester, Washington. Toxicity bioassays will be conducted by Nautilus Environmental in Fife, Washington. Periphyton analysis will be conducted by an accredited laboratory yet to be determined.

The expected range of results and laboratory reporting limits and methods are shown in Table 9.

Table 9. Expected Range of Results, Laboratory Reporting Limits, and Analytical Methods.

Analyte	Expected Range of Results	MEL Reporting Limits	Sample Preparation Method	Analytical Method
Periphyton	N/A	N/A	WDEQ, 2005	
Water Chemistry[1]				
Lead - TR	0.1 – 300 ug/L	0.1 ug/L	Field preserve; laboratory HNO_3/HCl digest	EPA 200.8
Copper - TR	0.1 – 10 ug/L	0.1 ug/L		
Lead - Diss	0.1 – 300 ug/L	0.1 ug/L	Field filter and preserve; laboratory HNO_3/HCl digest	
Copper - Diss	0.1 – 10 ug/L	0.1 ug/L		
Hardness	10 – 50 mg/L	0.3 mg/L	Field preserve	EPA 200.7
TSS	<1 – 50 mg/L	1 mg/L	N/A	EPA 160.2
Water Toxicity Bioassays[2]				
48-hr Daphnid	N/A	N/A	EPA-821-R-02-012 & Marshall, 2008	
7-day Trout	N/A	N/A	Lazorchak and Smith, 2007 & Marshall, 2008	

[1] = Information taken from the Manchester Laboratory Users Manual (MEL, 2008).
[2] = Personal communication with Nautilus Environmental.
TR = total recoverable.
Diss = dissolved.

Bioassays

Toxicity bioassays will follow the methods referenced above in Table 9 and will be conducted in the laboratory.

The 48-hour acute test will be conducted with *Daphnia pulex/magna*. A minimum of 5 organisms are put into a testing chamber and at least 4 replicates (chambers) are tested. The endpoint is survival, and at least 90% survival of the control sample is required.

Oncorhynchus mykiss (rainbow trout) is used for the 7-day survival and growth test. A minimum of 5 organisms are put into a testing chamber, and at least 4 replicates (chambers) are tested. Organisms are fed daily and illuminated daily for at least 16 hours followed by 8 hours of

darkness. Test endpoints include survival rate and growth of the survivors. A 90% survival of the control organisms is required.

Analytical Costs

Laboratory costs for toxicity testing, periphyton, and water chemistry are shown in Tables 9 and 10. The total combined cost for the study is $11,739.

Table 10. Laboratory Costs for Toxicity Bioassays and Periphyton.

Analyte	No. of Samples	Analysis Cost Per Sample	Subtotal
48-hr Daphnid	4	450	1800
7-day Trout	4	2000	8000
Periphyton	2	300	600
		Total Cost:	$10,400

Table 11. Laboratory Costs for Water Chemistry.[1]

Analyte	No. of Samples[2]	No. of Blanks[3]	No. of Field Replicates	Total No. of Samples	Analysis Cost Per Sample	Subtotal
Lead and copper - TR	4	1	2	7	67[a]	469
Lead and copper - Diss	4	2	2	8	84[b]	672
Hardness	4	0	2	6	22	132
Total suspended solids	4	0	2	6	11	66
					Total Cost:	$1,339

[1] = costs include 50% discount for analyses performed by MEL.
[2] = one sample at each of the two sites sampled twice for the project = 4 samples total.
[3] = blanks include both field and filter blanks.
[a] = includes cost of acid preservative.
[b] = includes cost of acid preservative and pre-cleaned filter.
TR = total recoverable.
Diss = dissolved.

Quality Control Procedures

Field

The field sampling procedures described in the *Sampling Procedures* section of this Quality Assurance (QA) Project Plan will be carefully followed to avoid contamination of samples. A copy of the QA Project Plan will be taken into the field for reference.

Field quality control samples for the water chemistry samples will consist of replicates and blanks (Table 12). Replicates will include two samples collected within a few minutes of each other at the same location. Blanks will consist of reagent grade water prepared by MEL and placed in the appropriate sample containers, taken to the field during sample collection, and transferred to new bottles. Blanks for metals will include the same processing and preservation as regular samples.

Table 12. Field Quality Assurance for Water Chemistry Samples.

Analyte	Field Replicate	Field Blank
Lead and copper - TR	2/project (1 for each sampling event)	1/project
Lead and copper - Diss	2/project (1 for each sampling event)	2/project (1 for each sampling event)
Hardness	2/project (1 for each sampling event)	N/A
Total suspended solids	2/project (1 for each sampling event)	N/A

TR = total recoverable.
Diss = dissolved.
N/A = no analysis.

Laboratory

The laboratory quality control procedures routinely followed by MEL and the contract laboratories will be satisfactory for the purposes of this project. Laboratory quality control samples for the water chemistry analyses being conducted by MEL are shown in Table 13.

Table 13. Laboratory Quality Control Samples

Analyte	Method Blank	Laboratory Control Sample	Laboratory Duplicate	Matrix Spike and Matrix Spike Duplicate
Lead and copper - TR	1 per batch*	1 per batch	1 per batch	1 per batch
Lead and copper - Diss	"	"	"	"
Hardness	"	"	"	"
Total suspended solids	"	"	"	N/A

TR = total recoverable.
Diss = dissolved.
* = A batch is equivalent to 1 sampling event for the project. There will be 2 sampling events (batches) for the project, so the above quality control samples will be conducted twice.
N/A = not applicable.

As an indication of bias due to sample preparation, laboratory control samples which contain a known amount of the analyte will be analyzed. Matrix spikes will give an indication of bias in the analysis due to matrix effects. Analytical precision will be estimated by comparisons of laboratory duplicates and of matrix spike duplicates.

Data Management Procedures

Field data will be recorded in a field notebook. Relevant information will be carefully transferred to electronic data sheets.

The data packages from MEL and the contract laboratories will include case narratives discussing any problems encountered during analysis, corrective actions taken, and an explanation of data qualifiers. The project manager will then review the data packages to determine if analytical MQOs (laboratory control samples, laboratory duplicates, and matrix spikes) were met.

Randy Marshall of Ecology's Water Quality Program will review the bioassay data packages. He is an agency expert on water quality bioassays.

Data for the project will be entered into Ecology's Environmental Information Management System (EIM) database. Data entered into EIM follow a formal data review process where data is reviewed by the project manager, the person entering the data, and an independent reviewer.

Audits and Reports

MEL participates in performance and system audits of their routine procedures. The results of these audits are available on request.

The draft technical report for this study will be provided to the client, internal Ecology reviewers, external reviewers, and other interested parties by July 2010. The final technical report will be completed in September 2010 and will include the following elements:

- Information about the sampling locations, including geographic coordinates and maps.
- Descriptions of field and laboratory methods.
- Tables presenting all the data.
- Discussion of project data quality.
- Summary of significant findings.
- Recommendations for future follow-up work.

Upon completion of the study, all project data will be entered into Ecology's EIM database. Public access to electronic data and the final report for the study will be available on Ecology's internet homepage (www.ecy.wa.gov).

Data Verification

The project manager will review laboratory data packages and data verification reports. Based on these assessments, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

To determine if analytical MQOs have been met, the project manager will compare results of the field and laboratory quality control samples to MQOs. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects to determine if any values exceed the lowest concentration of interest.

Formal (third party) validation of the data will not be necessary for this project.

Data Quality (Usability) Assessment

After the data have been reviewed and verified, the project manager will determine if the data are useable for the purposes of the study. The project manager will review laboratory data by determining if analytical MQOs were met.

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Appendices

Appendix A. Glossary, Acronyms, and Abbreviations

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

Aquatic organism: An organism that lives in water for most or all of its life.

Analyte: Water quality constituent being measured (parameter).

Bioassessment: Assessing the quality or health of a defined area in the environment using biological organisms. An example would be measuring the presence and quantity of aquatic insects in a stream.

Bioassay: Standard biological test. Usually a laboratory test which exposes organisms to the medium of interest (e.g., amphipod exposure to sediment). Results indicate the toxicity of the medium to that particular organism.

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

Daphnid: A small planktonic crustacean between 0.2 and 5 mm in length. Daphnia are commonly referred to as water fleas. They live in aquatic environments including swamps, freshwater lakes, ponds, streams, and rivers.

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

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

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

Periphyton: A complex mixture of algae, cyanobacteria, microbes, and detritus that is attached to submerged surfaces in most aquatic environments.

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

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

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

Total suspended solids (TSS): Portion of solids retained by a filter.

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

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

Club	Gig Harbor Sportsman Club
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EAP	Environmental Assessment Program
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedures
TSS	Total Suspended Solids
WAC	Washington Administrative Code
WRIA	Water Resources Inventory Area

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
mg/L	milligrams per liter (parts per million)
µg/L	micrograms per liter (parts per billion)

Appendix B. Periphyton Method

Draft Washington State Standard Operating Procedure for the Collection of Periphyton

Introduction

Periphyton are benthic algae that live attached or in close proximity to various substrates associated with the stream bottom. The structure, diversity, and abundance of periphyton is highly dependent on the diversity and availability of substrates in the stream. Periphyton algae often form visible filaments or colonies in the form of mats or biofilms attached to substrate.

Two basic types of periphyton are found in Washington streams: diatoms (Division *Chrysophyta*, Class *Bacillariophyceae*) and soft-bodied algae. Soft-bodied algae are represented by four major divisions: green algae (*Chlorophyta*), blue-green algae (*Cyanophyta*), gold/brown algae (*Chrysophyta*) and occasionally red algae (*Rhodophyta*).

Periphyton are important primary producers and chemical modulators in stream ecosystems. As such, periphyton can be more sensitive to certain stressors such as nutrients, salts, sediment, and temperature compared to other aquatic organisms. Measures of periphyton structure, diversity, and density are useful in the assessment of biological condition for surface waters. For more information on periphyton and their use in bioassessments, refer to Barbour et al. (1999) and Stevenson et al. (1996).

Sampling Time - Index Period

The recommended sample period for periphyton follows the sample period for benthic macroinvertebrates (see *Macroinvertebrate Sampling Index Period Standard Operating Procedure* (SOP)). It may be necessary to sample outside the recommended index period to coincide with flows in ephemeral, intermittent, or dewatered streams.

Sampling Methods - Field Procedure

The field procedure(s) for collecting periphyton will vary depending on the chosen targeted habitat. The targeted habitat represents the most common and stable habitat in the stream reach. Field selection of the targeted habitat where samples are collected will be based on the following prioritization: (1) riffles with dominant coarse substrate (Epilithic habitat); (2) woody snags in streams with dominant fine-grained substrate (Epidendric habitat); (3) organically rich pea gravel/sand (Epipsammic habitat) or (4) organically rich silt (Epipelic habitat) depositional areas along stream margins, and (5) emergent or (6) submerged vegetation (Epiphytic habitat).

Field staff will ensure that all equipment and supplies needed to conduct the periphyton sampling and subsequent subsample processing are assembled and ready for use.

Required items include:

Aluminum foil
Digital caliper
Distilled or deionized water
Dry ice
Envelopes
Filtration apparatus that includes hand pump (with gage), tubing, filter base, and filter funnel.
Forceps
Funnel
Glass microfiber filters (47 mm @ 0.7 micron)
Graduated cylinders
Hand saw (folding)
Labels
Lugol's solution
Pens and permanent markers
Plastic beaker (500 mL)
Plastic petri dishes (47 mm)
Plastic sample bottles (500 & 1000 mL Nalgene®)
Plastic tape (electrical preferable)
Plastic trays
Pocket calculator
Pruning shears
Ruler (with metric increments)
Scissor
Sealable plastic bags
Spatula
Serological volumetric pipettes (10 mL disposable) with rubber bulb
Toothbrush (soft and firm bristled)
Top-setting or survey rod

Sampling Method for Epilithic (Coarse Substrate) Habitats

1. Randomly select eight sampling locations within the riffle. If also sampling for macroinvertebrates using a Surber sampler, samples will be collected in close proximity to (but not within) the randomly selected Surber sample locations. See *Macroinvertebrate Sampling SOP* for description of selecting random sample locations.

2. Carefully remove one or two rocks from each of the eight randomly selected sample locations while retaining the rock's orientation as it occurred in the stream to avoid loss of periphyton. Rocks should be relatively flat and range in size from about 4 cm (coarse gravel) to 10 cm (small cobble) in diameter. Collect only one rock per randomly selected sample location if the diameter of the first rock selected is equal to or exceeds 7.5 cm. If the diameter of the first rock selected is less than 7.5 cm, select a second rock. If possible, select rocks that are similar with respect to size, depth, and exposure to sunlight. A total of eight to 16 rocks are collected at each sample site.

Gently place the rocks (as they were oriented in the stream) in a plastic tray; do not stack rocks upon one another. Transport the tray to a convenient sample-processing area. Where possible, process the sample out of direct sunlight to minimize degradation of chlorophyll.

3. Measure water depth and velocity at each of the eight locations using a topsetting rod and velocity meter and record on the datasheet. *Note:* Additional measurements of depth and velocity are not required if the sampler is already measuring these parameters for the macroinvertebrate sample. Assuming the sun is directly overhead, determine the relative degree of riparian shading (e.g. shaded, partial, or full sun) at each randomly selected sample location and record on the datasheet.

4. Scrub only the upper surface of each rock with a firm-bristled toothbrush using a circular motion. In circumstances where rocks are much greater than 10 cm (medium to large cobbles), firmly brush only a portion of the upper rock surface around 10 cm in diameter. Do not brush the sides or bottom of rocks. If needed, remove any filamentous algae and mosses by scraping with a knife and place in a separate plastic tray. Use a knife or scissor to cut algal filaments or moss into roughly 2 to 3 mm segments. Gently brush other larger plant material that may be attached to the rocks but do not collect the plants.

   Rinse the sampled rock surface, attached plants, and toothbrush bristles with a rinse bottle containing deionized or distilled water. Use rinse water sparingly, but be thorough. Collect rinsate in the plastic tray containing any filamentous algae or mosses. Repeat for the remaining rocks. Keep the sample volume less than 500 mL. After sample processing is complete, measure and record the total rinsate volume (now considered the composite sample volume) on the datasheet and pour the rinsate through a funnel into a 500 mL Nalgene® sample bottle.

5. For each rock processed, cover the surface with a sheet of aluminum foil. Either trim the foil with a knife or fold the foil to match the area sampled. Place the trimmed/folded foil templates into a labeled collection envelope and attach to the field data sheets.

6. Process the composite sample following steps described in *Subsample Processing Procedures* to extract subsamples for chlorophyll *a* analysis and taxonomic identification.

Sampling Method for Epidendric (Woody Snag) Habitats

Collecting quantitative microalgal periphyton samples from epidendric habitats presents a challenge because they generally have an irregular surface and are difficult to remove without loss of periphyton biomass. Use the following method to address these difficulties when sampling epidendric habitats:

1. Select a total of eight pieces of woody snag material from the same number of different locations throughout the reach. Select pieces greater than 1 cm in diameter that have likely been submerged for most of the year to allow for sufficient periphyton colonization but which are not smothered by bottom sediments.

2. Carefully remove an approximately 10 to 20 cm long section of each woody snag with pruning shears or a hand saw and place in a plastic tray. Transport the tray to a convenient sample-processing area. Where possible, process the sample out of direct sunlight to minimize degradation of chlorophyll.

3. Measure water depth and velocity at the point where each of the eight woody snags were removed using a top-setting rod and velocity meter and record on the datasheet. Assuming the sun is directly overhead, determine the relative degree of riparian shading (e.g. shaded, partial, or full sun) at each of the eight samples.

4. Scrub the entire surface of the woody section with a firm-bristled toothbrush. If needed, remove any filamentous algae and mosses by scraping with a knife and place in a separate plastic tray. Use a knife or scissor to cut algal filaments or moss into roughly 2 to 3 mm segments. Rinse the toothbrush and the section of wood with a rinse bottle containing deionized or distilled water. Use rinse water sparingly, but be thorough. Collect rinsate in the plastic tray containing any filamentous algae or mosses. Set the section of wood aside. Repeat for the remaining woody sections. Keep the sample volume less than 500 mL. After sample processing is complete, measure and record the total rinsate volume (now considered the composite sample volume) on the datasheet and pour the rinsate through a funnel into a 500 mL Nalgene® sample bottle.

5. Process the composite sample following the steps described in *Subsample Processing Procedures* to extract subsamples for chlorophyll *a* analysis and taxonomic identification.

Sampling Method for Epipsammic (Pea gravel/Sand) and Epipelic (Silt) Habitats Quantitative: Microalgal periphyton samples are collected from the upper 5 to 7 mm layer of epipsammic (pea gravel _ 5 mm/sand) and epipelic (silt) habitat in organically-rich depositional areas of the reach. Use the following method to sample epipsammic or epipelic habitats:

1. Select a total of five locations, in shallow organically-rich depositional zones that consist of either pea gravel, sand or silt substrate. NOTE: All five locations must be from the same type of habitat, either pea gravel/sand or silt.

2. At each location, hold the lid of a plastic Petri dish (47-mm diameter) upside down in the water; gently stir/shake the lid to remove air bubbles without disturbing the substrate.

3. With the lid still submerged, turn the inside of the lid toward the substrate that will be sampled without disturbing the substrate.

4. Carefully and slowly press (in cookie cutter fashion) the lid into the substrate.

5. Slide the lid onto a spatula to enclose the discrete collection. Holding the Petri dish firm against the spatula, carefully wash extraneous sediment from the spatula and lift out of the water.

6. Transport the Petri dish and spatula to a convenient sample-processing area. Where possible, process the sample out of direct sunlight to minimize degradation of chlorophyll.

7. Invert the lid and remove the spatula. Be careful not to lose any of the discrete sample still adhering to the spatula.

8. Rinse the substrate from the lid and spatula with a rinse bottle containing deionized or distilled water into a 500 mL Nalgene® sample bottle. Use rinse water sparingly, but be thorough. Combine all five discrete sample collections in the 500 mL Nalgene® sample bottle. Repeat at the remaining sample locations. Keep the sample volume less than 500 mL. After sample processing is complete, measure and record the total rinsate volume (now considered the composite sample volume) on the datasheet.

9. The total sample surface area for all five discrete samples collected with a 47-mm Petri dish is 85 cm2. Record the sampled surface area on the datasheet.

10. Measure water depth and velocity at the point where each of the five discrete collections were removed using a top-setting rod and velocity meter, and record on the datasheet. Assuming the sun is directly overhead, determine the relative degree of riparian shading (e.g. shaded, partial, or full sun) at each of the five sample locations and record on the datasheet.

11. Process the composite sample following the steps described in *Subsample Processing Procedures* to extract subsamples for chlorophyll *a* analysis and taxonomic identification.

Subsample Processing Procedures

Each composite sample processed in the field is used to extract subsamples for chlorophyll *a* analysis and taxonomic identification. Successful execution of subsample processing procedures described here is dependent on measuring and tracking the various volumes as the composite sample is processed. One subsample is extracted from each composite sample for the purpose of determining chlorophyll *a* in the laboratory. The remaining volume of the composite sample is considered the ID subsample and is preserved for taxonomic identification.

Subsampling processing procedures for periphyton composite samples are as follows:

1. In an area out of direct sunlight, assemble the filtration apparatus by attaching the filter base with rubber stopper to the filtration flask. Join the flask and a hand-operated vacuum pump (with pressure gage) using a section of tubing.

2. Place a 47-mm 0.7-micron glass microfiber filter (for example, Whatman® GF/F) on the filter base and wet with deionized or distilled water. *Note*: Wetting the filter will help it adhere to the base in windy conditions. Attach the filter funnel to the filter base.

3. Prior to subsample extraction, homogenize the composite sample by vigorously shaking or using a battery-powered stirrer for 30 seconds.

4. Extract one 10 mL aliquot of homogenized composite sample using a disposable serological volumetric glass pipette and dispense onto the middle of the wetted glass microfiber filter.

5. Filter the aliquot with the vacuum pump using 7 to 10 psi.

    a. Examine the filter. An adequate amount of periphytic biomass for analysis is indicated by the green or brown color of material retained on the filter. If needed, extract additional 5 mL aliquots and filter until a green or brown color on the filter is apparent. NOTE: For composite samples with abundant organic material and/or fine sediment, filtration of a 10 mL aliquot may not be possible. In these circumstances, filter one 5 mL aliquot. If no difficulties were apparent when filtering the first 5 mL aliquot, proceed with filtering a second 5 mL aliquot.

    b. The filtered aliquot(s) represent the chlorophyll a subsample. Determine the number of aliquots filtered and record the chlorophyll a subsample volume on the datasheet. For example, 2 aliquots x 5 mL/aliquot = 10 mL subsample volume.

    c. Rinse the sides of the filter funnel with deionized or distilled water, allow the water to be vacuumed completely before releasing the vacuum from the filtering apparatus.

    d. Using forceps, fold the filter into quarters with the filtered biomass inside. Remove the filter from the funnel base with forceps and wrap in a small piece of aluminum foil. Place the aluminum foil wrapped filter in a separate 47 mm Petri dish.

    e. Seal the sides of the Petri dish with plastic tape, and label the Petri dish with the following required information:

        - Site name
        - Sample ID
        - Collection date (mm-dd-yyyy)
        - Collection Time (24 hr.)
        - Composite sample volume (mL)
        - Subsample volume (mL)

    f. Repeat the aliquot extraction and filtration processes if necessary for quality control duplicates.

    g. Insert the labeled Petri dish(s) in a resealable plastic bag and place in a cooler containing dry ice. About 4.5 kg (10 pounds) of dry ice is needed for a small cooler (< 2 gal). Insulate the cooler with newspaper to minimize sublimation of dry ice. *Note*: Wet ice can be used if dry ice is not available. Make a note on the data sheet when wet ice is used.

    h. Coolers should be shipped within a few days after the subsamples have been prepared because of a 25 day holding time limit. Subsamples can be temporarily stored in a freezer (at -20°C) at the field office over weekends. Contact laboratory personnel to notify them of plans to ship (via overnight shipping service) coolers containing dry ice and frozen subsamples. Make sure you disclose to the carrier the amount of dry ice in the cooler prior to shipping.

6. Measure the volume of the remaining composite sample (which represents the ID subsample volume) and record on the datasheet.

7. Preserve the ID subsample with 5 to 10 percent Lugol's solution (see Sample Preservative-Lugol's Solution for preparation). Five percent should be sufficient for most samples, although up to 10 percent can be used for samples rich in organic matter. Record the preservative volume on the datasheet. The quantities of Lugol's solution required for selected sample volumes are:

   500 mL ID subsample, add 25 mL Lugol's solution
   400 mL ID subsample, add 20 mL Lugol's solution
   250 mL ID subsample, add 12 mL Lugol's solution

8. Label the ID subsample with the following required information:
   - Site name
   - Sample ID
   - Collection date (mm-dd-yyyy)
   - Collection time (24 hr.)
   - ID subsample volume (mL) [ID subsample + preservative]

Sample Preservative - Lugol's Solution

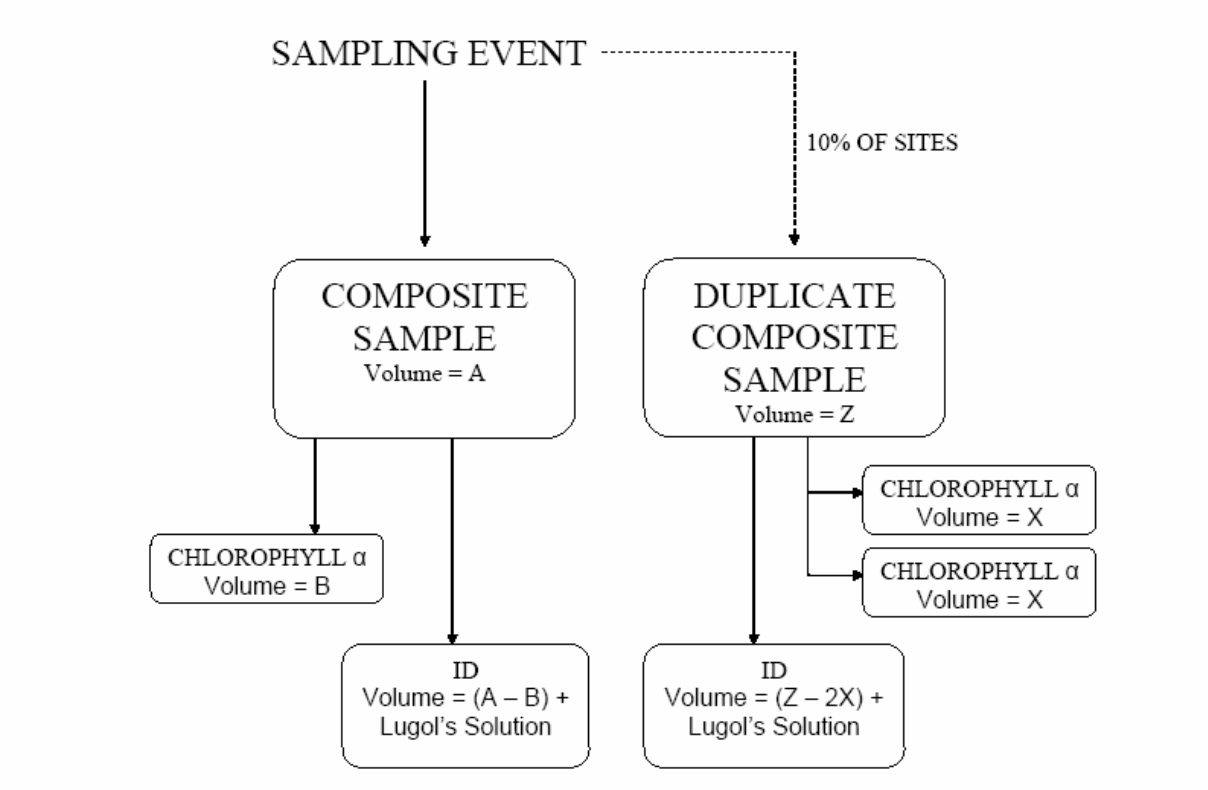
Prepare Lugol's solution by dissolving 20 grams potassium iodide (KI) and 10 grams iodine crystals in 200 mL distilled water containing 20 mL glacial acetic acid. Store Lugol's solution in an opaque plastic bottle.

Quality Control

Following the processes described under Sampling Methods-Field Procedures, at least ten percent (10%) of all collected composite samples must consist of duplicate composite samples (e.g., 2 duplicates for 11 to 20 samples, 3 duplicates for 21 to 30 samples). Duplicate composite sampling consists of two samplers each with the same equipment, collecting simultaneously alongside (1) randomly selected locations for Epilithic samples, (2) woody snag locations for Epidendric samples, (3) shallow depositional locations for Epipsammic/Epipelic samples, or (4) locations of emergent or submerged vegetation for Epiphytic samples.

Following the processes described under Subsample Processing Procedures, the sampler who collected the duplicate composite sample extracts two chlorophyll *a* subsamples from the duplicate composite sample. The remaining duplicate composite sample volume will be used for the duplicate ID subsample. Duplicate composite samples are collected to check the variability between field samplers while the two duplicate chlorophyll *a* subsamples provide an indication of precision and the quality of the duplicate composite sample homogenization.

An illustration of the duplicate composite sample/subsample processes is provided below:



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