Quality Assurance Project Plan

Des Moines, Massey, and McSorley Creeks Copper and Zinc Water Quality Assessment

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Waterbody Numbers:

Des Moines Creek	LLID 1223268474050, WA-09-2000
Des Moines Creek East Tributary	LLID 1223059474260
Massey Creek	LLID 1223259473968
McSorley Creek	LLID 1223235473729

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NWRO – Northwest Regional Office
EAP - Environmental Assessment Program
EIM - Environmental Information Management system

Table of Contents

Abstract

A five-year study conducted for the city of Des Moines (1995-1999) reported that Des Moines Creek, Massey Creek, and McSorley Creek violated water quality criteria for dissolved copper and zinc (copper only for McSorley) during storm events. These data led to the listing of the 3 streams under Section 303(d) of the federal Clean Water Act as water quality impaired. Because the data are more than five years old and many changes in stormwater management have occurred within these watersheds, updated information is required to verify the need for a Total Maximum Daily Load (water cleanup plan) analysis.

The Washington State Department of Ecology (Ecology) will conduct a water quality study in Des Moines, Massey, and McSorley Creeks to determine existing conditions. Levels of copper and zinc during both baseflow and storm events will be determined. If study data indicate levels higher than the water quality standards,[1] the needed reductions in existing copper and zinc loads from potential sources will be determined.

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.

[1] Chapter 173-201A-240(3) Washington Administrative Code (WAC)

Background

Des Moines, Massey, and McSorley Creeks are small urban streams located in King County, south of SeaTac International Airport (Figure 1). These streams together drain much of the city of Des Moines. In addition, they provide drainage to portions of the cities of SeaTac, Kent, and Federal Way. The streams flow through mostly residential and commercial areas before discharging into central Puget Sound. However, the lower reach of Des Moines Creek and McSorley Creek flow through Des Moines Creek Park and Saltwater State Park, respectively.

These streams serve as habitat for many salmonids (i.e., Chinook, coho, chum, and pink salmon, steelhead, and coastal cutthroat trout). In addition, other resident species, such as cutthroat and rainbow trout, pumpkinseed, sunfish, largemouth bass, bluegill, bullheads, and sculpins, have been observed (BioAnalyst, 1999). Currently these streams are receiving restoration efforts to improve fish habitat.

Past data indicated levels of copper and zinc in these 3 streams were higher than the Washington State acute water quality criterion during storm events. For urban streams, there is concern that copper and zinc in stormwater runoff may contribute to pre-spawn mortality among adult coho salmon.

The most recent data on copper and zinc levels in these streams are over 9 years old. Updated data are needed to (1) determine if copper and zinc are still exceeding water quality standards during storm events and (2) estimate any needed load reductions.

A long-term monitoring study (1995 to 1999) found dissolved copper and zinc during baseflows in the dry season (June to September) did not exceed water quality standards (Herrera, 2001). However, during storm events in the wet season (October to May), the levels of copper and zinc were high and often exceeded standards.

Table 1 shows the mean and range of copper and zinc concentrations reported in the Herrera (2001) study for Des Moines, Massey, and McSorley Creeks.

Herrera (2001) monitored 25 storm events during their study. Des Moines Creek exceeded the acute water quality standards for copper in 12 samples and for zinc in 2 samples. Massey Creek exceeded acute standards for copper in 10 samples and for zinc in 8 samples. McSorley Creek exceeded acute standards in for copper in 5 samples and none for zinc. The Herrera study reported data for 2 sites in Des Moines and McSorley Creeks, and 4 sites in Massey Creek.

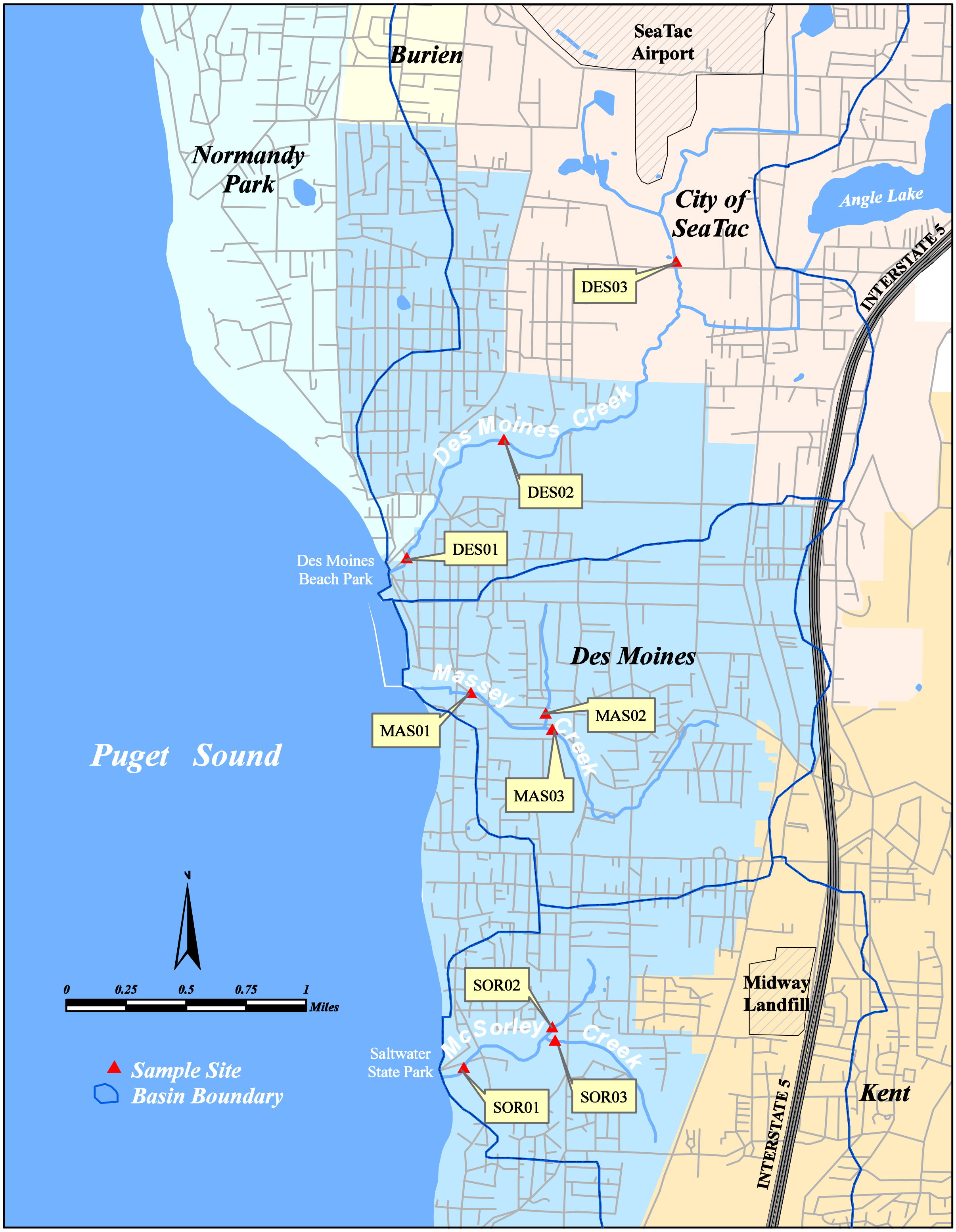

Figure 1. Study area and sample sites for the Des Moines Creek basin copper and zinc study.

Table 1. Historical copper, zinc, hardness, and flow results (Herrera, 2001), plus acute water quality criteria from Des Moines, Massey, and McSorley Creeks (mean and range).

Parameter	Baseflow (Mean and Range)			Storm Flow (Mean and Range)		
	Des Moines	Massey	McSorley	Des Moines	Massey	McSorley
Acute WQ Criteria (*ug*/L)[1]	Cu=10.2–24.8 Zn=72.6-160	Cu=15.9-23.2 Zn=108-151	Cu=13.4-21.8 Zn=92.2-143	Cu=4.6-14.8 Zn=35.4-101	Cu=3.6-19.1 Zn=28.1-127	Cu=5.6-16.2 Zn=42.1-109
Copper dissolved (*ug*/L)	2.8 (1.0U-14.8)	1.6 (1.0U-11.6)	2.8 (1.0U-3.4)	3.2 (2.9-6.0)	4.4 (1.0U-35.6)	6.3 (1.2-52.4)
Zinc dissolved (*ug*/L)	7.5 (3.0U-66.0)	2.3 (3.0U-14.0)	2.0 (3.0U-4.5)	18.3 (3.0U-78.0)	17.3 (3.0U-109)	11.7 (3.0U-57.0)
Hardness (mg/L)	93.8 (58.4-149)	110 (93.1-139)	96.4 (77.5-130)	49.1 (25.0-86.2)	47.3 (19.1-113)	51.4 (30.7-94.9)
Flow (cfs)[2]	1.45 (0.85-2.30)	2.24 (1.40-3.40)	0.27 (0.03-0.52)	15.4 (3.5-39.4)	9.70 (2.50-27.2)	3.60 (0.20-8.40)

1 = Acute water quality criteria using hardness data per Chapter 173-201A WAC were calculated from Herrera (2001).
2 = Flow statistics reported for the most downstream site in each basin.
U = Analyte not found at the detection limit shown.

Water Quality Criteria

The state water quality standards for copper and zinc require analysis of the dissolved form - the portion that is most available to biological uptake. Analysis of hardness (mg/L as $CaCO_3$) is also required to determine the toxicity of copper and zinc. It's used as a means to estimate the cationic/anionic and humic acid binding potential of these metals which may limit toxicity.

The state of Washington, under the federal Clean Water Act, promulgated standards to evaluate dissolved copper and zinc toxicity (WAC 173-201A, 2006).

Copper
- Acute standard violation if concentration is $>(0.96)(e^{(0.9422*[\ln(\text{hardness})]-1.464)})$.
- Chronic standard violation if concentration is $>(0.96)(e^{(0.8545*[\ln(\text{hardness})]-1.465)})$.

Zinc
- Acute standard violation if concentration is $>(0.978)(e^{(0.8473*[\ln(\text{hardness})]+0.8604)})$.
- Chronic standard violation if concentration is $>(0.986)(e^{(0.8473*[\ln(\text{hardness})]+0.7614)})$.

The Washington State water quality standards for toxic metals require both acute and chronic criteria to be met. The acute standard is based on a 1-hour average concentration not to be exceeded more than once every 3 years on the average. Likewise, the chronic standard is a 4-day average concentration not to be exceeded more than once every 3 years on the average (Chapter 173-201A-240, WAC).

For a waterbody to be 303(d) listed for toxic substances, 2 or more samples within a 3-year period must exceed the numeric state water quality criteria or the National Toxics Rule criteria.

Potential Sources of Copper and Zinc Contamination

Copper and zinc are 2 heavy metals commonly found in stormwater runoff. Many of the pollutants in stormwater are associated with automobile use and maintenance (Pitt and Lalor, 2000). The wear from brake lining is thought to be a significant source of copper in stormwater. In addition, tire wear, fluid leaks, and air deposition from car exhaust also contribute to the pollutant pool in stormwater (Golding, 2006). Other potential sources of copper to surface waters include copper pesticides; air emissions from fuel combustion, industry, and wood burning; soil erosion; landfills; treated wood products; domestic water discharged to drains; and architectural copper (i.e., roofs, gutters, and copper treated shingles).

Common sources of zinc in urban settings are rooftops; streets and highways; galvanized metal including scrap; and air deposition. Other sources of zinc in stormwater include particles from tires (1% by weight) and pavement wear; auto exhaust; and culvert and pipes (Golding, 2006).

Galvanized metal is a significant source of zinc to surface waters. Roof runoff is known to carry large loads of zinc during storm events, from galvanized roof components. Many roofs have gutters and downspouts made with zinc. In industrial areas, galvanized gutters, downspouts, and heating and cooling components on roofs are considered the leading source of zinc (60%), while residential roofs are less significant (7%) (Wisconsin DOT, 1997). Corrosion of galvanized roofs can be exacerbated in marine environments.

Project Description

This study will evaluate copper and zinc concentrations in Des Moines, Massey, and McSorley Creeks during baseflows in the dry season and during storm events in the wet season. Two samples will be collected during baseflows. Three storm events will be targeted, and samples will be collected during the rising limb of the hydrograph. Sampling a storm event will occur only after being preceded by a 24-hour period of dry weather.

Sample sites will be the same during baseflows and storm events. For each stream, sampling will be conducted at one downstream site, as close to the mouth as possible while avoiding marine influences. Sampling will also occur at two upstream locations to isolate major tributaries and assess the upper watersheds.

Samples collected during storm events will be hand composited. Two sub-samples will be collected for each one-hour composite sample, at the beginning and at the end of the hour.

Des Moines, Massey, and McSorley Creeks all support salmonids. Pre-spawn mortality of adult coho salmon has been observed in Des Moines Creek. There is growing concern that stormwater runoff, which can include copper and zinc, may be contributing to pre-spawn mortality. The most recent data on copper and zinc for the 3 study streams are 9 years old. The data generated from this project will be used to assess metals concentrations compared to water quality criteria and the state 303(d) list. Furthermore, habitat and stormwater management improvements in the 3 watersheds over the past years require an assessment of current conditions.

Objectives

Objectives of the study are to:

- Provide a verification of the status of 303(d) listings for copper and zinc in Des Moines, Massey, and McSorley Creeks.
- If data warrant, estimate copper and zinc loading reduction targets needed to meet Washington State water quality standards.

Organization and Schedule

The individuals listed in Table 2 are involved in this project. All are employees of the Washington State Department of Ecology. Table 3 shows the proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Table 2. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Randy Coots Toxics Study Unit SCS Phone (360) 407-6690	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, enters data into EIM, and writes the draft report and final report.
Steve Golding Toxics Study Unit SCS Phone (360) 407-6701	Co-Investigator	Provides technical support and assists with collection of storm event samples.
Chuck Springer Watershed Technical Support Unit, WOS Phone (360) 407-6997	Hydrologist	Develops discharge rating curves for Massey and McSorley Creeks and provides discharge information to the project lead for sample collection periods.
Dale Norton Toxics Study Unit SCS 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 SCS 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 WOS Phone (360) 407-6596	Section Manager for Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Sinang Lee Water Quality Program Northwest Regional Office Phone (425) 649-7110	Client	Clarifies scopes of the project, provides internal review of the 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
SCS – Statewide Coordination Section
WOS – Western Operations Section
EIM – Environmental Information Management system
QAPP – Quality Assurance Project Plan

Table 3. Schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	
Field work completed	April 2009
Laboratory analyses completed	May 2009
Environmental Information System (EIM) system	
EIM data engineer	Michael Friese
EIM user study ID	RCOO0009
EIM study name	Des Moines, Massey, and McSorley Creeks Copper and Zinc Water Quality Assessment
Data due in EIM	September 2009
Quality Assurance Plan	
Project Tracker code	09-195
Author lead	Randy Coots
Schedule	
Draft due to supervisor	September 2008
Draft due to client/peer reviewer	October 2008
Final report due on web	December 2008
Final report	
Author lead	Randy Coots
Schedule	
Draft due to supervisor	June 2009
Draft due to client/peer reviewer	July 2009
Final report due on web	September 2009

Quality Objectives

Manchester Environmental Laboratory (MEL) is expected to meet quality control (QC) requirements of methods selected for the project. QC procedures used during field sampling and laboratory analysis will provide estimates for determining accuracy of the monitoring data. Table 4 shows the measurement quality objectives (MQOs) for the analytical methods selected. Reporting limits are expected to be low enough to meet applicable criteria within budget limits and allow comparisons to 303(d) listing criteria (Ecology, 2002), www.ecy.wa.gov/programs/wq/303d/policy1-11Rev.html

Bias can be defined as systematic error due to contamination, sample preparation, calibration, or the analytical process. Most sources of bias can be minimized by adherence to established protocols for collection, preservation, transportation, storage, and analysis of study samples.

Precision is a measure of the ability to consistently reproduce results. Precision will be evaluated by analysis of check standards, duplicates/replicates, spikes, and blanks. Results of multiple analyses will be used as a means to estimate precision. Field replicates will be analyzed to estimate *overall precision* of the entire sampling and analysis process. Analysis of laboratory duplicates, which consist of aliquots from one sample container, will estimate *laboratory precision*. The difference between the precision estimate of the laboratory duplicates and the precision estimate of field replicates is an estimate of *field precision*.

Measurement Quality Objectives (MQOs) may be difficult to achieve for concentrations near the limits of detection. Relative accuracy will decrease when concentrations are near reporting limits. These data will be reviewed by MEL using Standard Operating Procedures (SOPs) for data qualification.

Table 4. Measurement Quality Objectives for analysis of water samples

Analysis	Check Standards/LCS (recovery)	Duplicates (RPD)	Matrix Spikes (recovery)	Matrix Spikes Duplicates (RPD)
Copper	85-115%	25%	75-125%	20%
Zinc	85-115%	25%	75-125%	20%
Hardness	85-115%	25%	75-125%	20%
TSS	80-120%	25%	NA	NA

LCS = laboratory control samples
RPD = relative percent difference
TSS = total suspended solids

Study Design

Overview

The study objectives will be met by characterizing copper and zinc concentrations and loads during baseflows and storm events in Des Moines, Massey, and McSorley Creeks. Levels of total and dissolved copper and zinc will be monitored at the mouths and two upstream sites of the study streams. A flow station run by the King County Hydrologic Center is currently active in Des Moines Creek. Flow will be monitored in Massey and McSorley Creeks by Ecology's Stream Hydrology Unit.

The study will use a fixed network of 3 sites within each of the 3 basins. Each site will be sampled 2 times during baseflow and during the rising limb of the hydrograph of the 3 synoptic storm events. The lowest downstream station in each creek will be located near discharge to Puget Sound, avoiding marine influences.

Details

Data from the fixed network will provide copper and zinc data sets to meet the following needs:

- Verify that copper and zinc concentrations in the 3 study streams still violate water quality standards, and determine if the state 303(d) listing for nonattainment of beneficial uses is justified.
- Provide an estimate of the copper and zinc loads and concentrations in the study streams during base and stormwater flows.
- Identify specific reaches or tributaries of concern by providing targeted data for prioritizing problematic areas.

For a waterbody to be 303(d) listed for toxic substances, 2 or more samples within a 3-year period must exceed the numeric Washington State water quality criteria or the National Toxics Rule criteria. The study schedule provides for 2 samples per site during baseflows.

Storm event sampling will be conducted during the rising limb of the hydrograph of 3 storms. Up to 3 one-hour composite samples will be submitted to MEL from each of 3 storms per site. Storm sampling will be initiated based on an increase in discharge following the onset of precipitation.

The water quality sample stations are listed in Table 5 and shown on Figure 1. The latitude and longitude of sample stations are provided in Appendix A. Stations were selected based on avoidance of marine influences, the ability to evaluate major tributaries, access, and dividing the 3 basins for prioritizing source areas.

Table 5. Sample sites in Des Moines, Massey, and McSorley Creeks[1].

Watershed/ Site ID	Location	Reason for Site
Des Moines Creek / DES01	Des Moines Creek Park near discharge to Puget Sound	Just above salt wedge includes whole basin
Des Moines Creek / DES02	Des Moines Creek just below Des Moines Wastewater Treatment Plant	Includes the WWTP, the restricted area south of SeaTac Airport, and Angle Lake
Des Moines Creek / DES03	Just below Tyee Golf Course at South 200th Street	Captures upper drainage from around SeaTac Airport
Massey Creek / MAS01	Above Marine View Drive	Above salt wedge includes most of basin
Barnes Creek / MAS02	Along Kent-Des Moines Road just above confluence	Isolates the major tributary to Massey Creek
Massey Creek / MAS03	Along Kent-Des Moines Road just upstream of confluence with Barnes Creek	Located mid-basin isolating the upper drainage
McSorley Creek / SOR01	Saltwater State Park near discharge to Puget Sound	Just above salt wedge includes whole basin
North Fork McSorley Creek / SOR02	Saltwater State Park upstream of confluence of the two forks	Isolates major tributary including discharge from Midway Landfill ponds
McSorley Creek / SOR03	Saltwater State Park upstream of confluence of the two forks	Located mid-basin isolating the upper drainage

[1]= Latitude and longitude of study sites provided in Appendix A.

Instantaneous dissolved copper and zinc loads will be estimated at each site using streamflow data. This will allow load estimates for individual streams and segments for evaluation of management priorities.

Continuous streamflow data will be obtained from a gaging station operated by King County Hydrologic Information Center (11d - Des Moines Creek below SR 509, Des Moines, near mouth). Real-time monitoring of King County's gaging station on Des Moines Creek will assist in triggering storm-event sampling. Ecology's Stream Hydrology Unit will install staff gages for streamflow and develop discharge rating curves for Massey and McSorley Creeks.

Storm monitoring

The purpose of storm-event monitoring is to better characterize the critical period for loading from potential sources of copper and zinc to Des Moines, Massey, and McSorley Creeks. Historical data show significantly higher copper and zinc loading during rain events.

Storm-event sampling will commence following recharge of groundwater and saturation of surface soils. This can be verified by small amounts of precipitation resulting in an increase of stage height.

Three storms will be sampled, with a storm event defined as a minimum 0.20 inch of rainfall in a 24-hour period preceded by no more than trace rainfall in the previous 24 hours. Rainfall of 0.5 inch or more in 24 hours occurs on average 26 times per year.

Storm sampling will consist of 3 teams each sampling 3 sites per stream. The rising limb of the hydrograph will be targeted for sampling. This will characterize the storm's highest potential for loading of copper and zinc over the storm event.

Streamflow will be estimated for Des Moines Creek using stage and rating curves developed by King County. Massey and McSorley Creeks streamflow will be estimated by stage height and discharge relationships developed by Ecology's Stream Hydrology Unit. Gages will be set at the upstream side of the box culvert at 10th Avenue for Massey Creek, and the upstream side of the road bridge into Saltwater State Park for McSorley Creek. For upstream sites, reference points will be established at sampling sites and a discharge relationship to the downstream site will be developed over the course of the study. Daily rainfall data will be obtained from local sources.

If it becomes necessary to make significant changes to the study, adjustments will be addressed through an addendum to the Quality Assurance Project Plan and sent to the appropriate parties.

Sampling Procedures

Table 6 lists the sample size, container, preservation, and holding time for each study parameter. Sample containers will be obtained from Manchester Environmental Laboratory.

Table 6. Sample containers, preservation, and holding times for study samples.

Parameter	Sample Size	Container	Preservative	Holding Time
Dissolved Cu/Zn*	500 mL	500 mL Teflon or HDPE	Filter 0.45 *u*m HNO_3 to pH<2	6 months
Total Cu/Zn	500 mL	500 mL Teflon or HDPE	HNO_3 to pH<2	6 months
Hardness	100 mL	125 mL poly	H_2SO_4 to pH<2	6 months
Turbidity	500 mL	500 mL poly	Cool to 4 ^oC	48 hours
TSS	1,000 mL	1,000 mL poly	Cool to 4 ^oC	7 hours

*= dissolved metals will be filtered in the field (0.45 *u*m) within 15 minutes of collection (MEL, 2008)

Sample sites will be located by a handheld global positioning system (GPS) and recorded in field books. Ecology's Environmental Assessment Program (EAP) standard operating procedures for *Determining Global Positioning System Coordinates* (Janisch, 2006)) will be followed. Any significant identifying structures relative to sample sites will be recorded in field books.

Procedures for collection of metal samples will follow guidance in EPA method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels* (EPA, 1995) and Ecology SOPs. Low-level metals procedures and clean-techniques will be employed according to Ecology's SOPs:

- Manually Obtaining Surface Water Samples (Joy, 2006).
- Collection and Field Processing of Metals Samples (Ward, 2007).

Historical data (Herrera, 2001) has shown dry season levels of copper and zinc to be low and requires low-level analysis to ensure detection. Dry season samples will be collected as single grabs following an extended dry period. The critical period for copper and zinc loading to study streams is during wet season storm events.

During the dry season, metal samples will be collected directly into 500 mL Teflon containers for low-level analysis and 500 mL HDPE containers for storm event samples. Dissolved metals samples will be filtered in the field using pre-cleaned 0.45 *u*m Nalgene filter units (#450-0045, type S) within 15 minutes of collection. The filtrate will be collected into a new pre-cleaned 500 mL Teflon container. Metal samples will be preserved in the field to pH <2 with 1:1 nitric acid provided by MEL in Teflon vials. Containers, Nalgene filters, and acid vials will be pre-cleaned by MEL, as described by Kammin et al. (1995), and sealed in plastic bags until used. Field staff will wear powder-free nitrile gloves during collection and filtering of samples.

Weather forecasts and satellite imagery will be monitored through the wet season for initiation of sample events. The minimum rainfall required to qualify for a storm event will be 0.2 inch over a 24-hour period preceded by no more than trace amounts of rainfall in the previous 24 hours. When predictions indicate a storm system exceeding 0.2 inch of rainfall within a 24-hour period will be in the study area, field teams will be deployed to each stream prior to the start of the storm. The first storm sample will be collected after rainfall begins and stream turbidity increases, or staff gages located at each stream raise 0.5 inches. Samples will be collected as hand grabs from mid-channel and composited.

Storm event sub-samples will be collected at the start and conclusion of one hour. Two consecutive one-hour sub-samples will be hand composited into a single one-hour average sample for submission to the laboratory. Stage height will be recorded for each subsample. Following each sample event, discharge data will be reviewed to assure composite samples were collected during the rising limb of the hydrograph. A total of 3 composite samples from each stream site will be submitted to the laboratory per storm event.

Following collection and filtration, composite samples will be placed in polyethylene bags in the field and placed in ice chests at 4^{o} C. After return from the field, sample ice chests will be put in a secure walk-in cooler at Ecology Headquarters, and transported to MEL the following day. All staff will follow chain-of-custody procedures throughout the sampling process (MEL, 2006).

Laboratory Measurement Procedures

All project samples will be analyzed at MEL. The laboratory may use other appropriate methods following consultation with the project lead.

Table 7 shows the expected range of results, sample preparation, and the analytical methods for the project. Metals samples will be analyzed by ICP/MS (Inductively Coupled Plasma Mass Spectrometer) using EPA Method 200.8. The MEL's reporting limits for copper (1.0 *u*g/L) and zinc (3.0 *u*g/L) will be adequate for identifying exceedance of water quality criteria. Table 1 shows the range of acute water quality criteria from the most recent samples collected from the study streams (Herrera, 2001).

Table 7. Analytical methods.

Analyte	Sample Type	Analysis	Expected Range of Results	Sample Preparation Method	Analytical Method
Copper	whole water	total recoverable	1 – 100 *u*g/L	HNO_3/HCl digest	EPA 200.8 ICP/MS
	filtered water	dissolved	1 – 100 *u*g/L	HNO_3/HCl digest field filtered and preserved	EPA 200.8 ICP/ MS
Zinc	whole water	total recoverable	10 – 1000 *u*g/L	HNO_3/HCl digest	EPA 200.8 ICP/MS
	filtered water	dissolved	10 – 700 *u*g/L	HNO_3/HCl digest field filtered and preserved	EPA 200.8 ICP/MS
Hardness	whole water	total	1 – 100 mg/L	NA	EPA 200.7 ICP
TSS	whole water	total	1 – 50 mg/L	NA	EPA 160.2
Turbidity	whole water	total	2 - 100 NTU	NA	SM 2130

TSS = total suspended solids
NA = not applicable
HNO_3 = nitric acid
HCl = hydrochloric acid
EPA = U.S. Environmental Protection Agency
ICP/MS = Inductively Coupled Plasma Mass Spectrometer
NTU = nephelometric turbidity units
SM = Standard Methods for the Examination of Water and Wastewater 20th Edition (APHA et al., 1998)

Quality Control Procedures

Field

Table 8 shows a list of field quality assurance (QA) samples and type to be analyzed for the project. The intent of QA samples is to provide an estimate of the total variability of each analysis, field plus laboratory. Field QA will consist of collection and analysis of replicate samples and filter blanks. Replicate samples are made up from two samples collected one after the other as close to the same time and location as possible. Filter blanks will consist of reagent grade water prepared by MEL and placed in Teflon containers. They are taken to the field during a sample event, filtered with other samples, transferred to a new clean Teflon container, acidified, and returned to MEL along with study samples.

Field staff will wear non-talc nitrile gloves during sample collection and filtration. Immediately following collection, samples will be stored in plastic bags in iced coolers, until delivered to MEL.

To help minimize field variability from sample collection, staff will be familiar with and follow methods described in EPA method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels* (EPA, 1995) and Ecology SOPs:

- Manually Obtaining Surface Water Samples (Joy, 2006).
- Collection and Field Processing of Metals Samples (Ward, 2007).

Table 8. Field quality assurance samples.

Analysis	Quality Assurance Samples
Field Replicates[1]	
Total Recoverable and Dissolved Copper	3/ project (1 TR and 1 dissolved for each storm event)
Total Recoverable and Dissolved Zinc	3/ project (1 TR and 1 dissolved for each storm event)
Hardness	1/study
Total Suspended Solids	1/study
Filter Blanks	
Dissolved Copper	3/ project (1 dissolved for each storm event)
Dissolved Zinc	3/ project (1 dissolved for each storm event)

TR = total recoverable
Replicates[1] = Two independent samples collected as close to the same time and location as possible.

Laboratory

The MEL will follow SOPs as described in the *Manchester Environmental Laboratory Quality Assurance Manual* (MEL, 2006). Laboratory quality control (QC) samples will include laboratory control samples, methods blanks, analytical duplicates, and matrix spikes and matrix spike duplicates. Types and frequencies of laboratory QC samples to be analyzed for the project are presented in Table 9.

Table 9. Laboratory quality control samples.

Analysis	Laboratory Control Sample	Standard Reference Material	Method Blank	Analytical Duplicate	Matrix Spikes and Spike Duplicates
TR and Dissolved Copper	1/batch	1/batch	1/batch	1/batch	1/batch
TR and Dissolved Zinc	1/batch	1/batch	1/batch	1/batch	1/batch
Hardness	1/batch	--	1/batch	1/batch	NA
Turbidity	1/batch	--	1/batch	1/batch	NA
Total Suspended Solids	1/batch	--	1/batch	1/batch	NA

TR = total recoverable

Study Budget

A summary of the sample numbers and laboratory costs are presented below in Tables 10 and 11. The total laboratory cost for the project is estimated at $24,902 (Table 11). All analyses will be conducted by MEL. The cost estimates reflect a 50% discount for analyses conducted by MEL.

Table 10. Summary of sample numbers.

Analysis	Monito-ring Sites	*Baseflow*			*Storm Events*			
		Baseflow Events	QA Samples	Total Baseflow Samples	Storm Events	Samples Per Event	QA Samples	Total Storm Event Samples
Diss Cu, Zn	9	2	2	20	3	3	6	87
TR Cu, Zn	9	2	2	20	3	3	6	87
Hardness	9	2	2	20	3	3	6	87
Turbidity	9	2	2	20	3	3	6	87
TSS	9	2	2	20	3	3	6	87

QA = quality assurance
Diss = dissolved
Cu = copper
Zn = zinc
TR = total recoverable
TSS = total suspended solids

Table 11. Summary of laboratory costs.

Baseflow			
Analysis	Cost/ Sample	Total Samples[1]	Subtotal
Metals*	$218	20	$4,360
Hardness	$22	20	$440
Turbidity	$11	20	$220
TSS	$11	20	$220
		Total	$5,240
$58 x 2 (TR & diss) analysis + $30 prep + $27 filter + $18 x 2 teflon bottles + $9 preservative = $218 per metals sample.			
Storm Event			
Analysis	Cost/ Sample	Total Samples	Subtotal
Metals*	$182	87	$15,834
Hardness	$22	87	$1,914
Turbidity	$11	87	$957
TSS	$11	87	$957
		Total	$19,662
		Grand Total	$24,902
$58 x 2 (TR & diss) analysis + $30 prep + $27 filter + $9 preservative = $182 per metals sample.			

1 = Totals include QA samples
*Metals estimates for 1 total recoverable and 1 dissolved per sample.
TR = total recoverable
diss = dissolved
TSS = total suspended solids

Data Management Procedures

All field data and observations will be recorded in notebooks on waterproof paper. The information contained in field notebooks will be transferred to Excel spreadsheets after return from the field. Data entries will be independently verified for accuracy by another member of the project team.

Case narratives included in the data package from MEL will discuss any problems encountered with the analyses, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers. Laboratory QC results will also be included in the data package. This will include results for surrogate recoveries, laboratory duplicates, matrix spikes, and laboratory blanks. The information will be used to evaluate data quality, determine if the MQOs were met, and act as acceptance criteria for project data.

Field and laboratory data for the project will be entered into Ecology's Information Management System (EIM). Laboratory data will be downloaded directly into EIM from MEL's data management system (LIMS).

Audits and Reports

MEL participates in performance and system audits of their routine procedures. Results of these audits are available upon request.

A draft report of the study findings will be completed by the project lead in July 2009 and a final report in September 2009. The report will include, at a minimum, the following:

- A map showing all sampling locations and any other pertinent features to the study area.
- Coordinates of each sample site.
- Description of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered.
- Summary tables of the chemical and physical data.
- Results of the copper and zinc related to recommended standards and load reduction targets.
- A presentation of significant findings which includes an evaluation of the current 303(d) status for study streams.
- Complete set of chemical and physical data and MEL QA review in the Appendix.

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

Data Verification

Data verification is a process conducted by those producing data. Verification of laboratory data is normally performed by a MEL unit supervisor or an analyst experienced with the method. It involves a detailed examination of the data package using professional judgment to determine whether the MQOs have been met. Final acceptance of the project data is the responsibility of the project lead. The complete data package, along with MEL's written report, will be assessed for completeness and reasonableness. Based on these assessments, the data will either be accepted, accepted with qualifications, or rejected and re-analysis considered.

Data verification involves examining the data for errors, omissions, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages, including QC results for dissolved and total recoverable copper and zinc analysis conducted by MEL, will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review. MEL staff will provide a written report of their data review which will include a discussion of whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions. All data generated from the project will be entered into the EIM database.

Data Quality (Usability Assessment)

After the project data have been reviewed and verified, the project lead will determine if the data are of sufficient quality to make decisions for which the study was conducted. The data from the laboratory's QC procedures, as well as results from field replicates and laboratory duplicates and surrogate recoveries, will provide information to determine if MQOs have been met. Laboratory and QA staff familiar with assessment of data quality may be consulted. The project final report will discuss data quality and whether the project objectives were met. If limitations in the data are identified, they will be noted.

Some analytes will be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of field replicates, along with laboratory QC results. This will include an assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and the success of laboratory QC samples meeting control limits.

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Appendix A. Samples Site Latitude and Longitudes

Table 12. Latitude and longitude of sampling sites.

Stream/Sample site	Latitude	Longitude
Des Moines Creek		
DES01	47.40584	-122.32764
DES02	47.41178	-122.32032
DES03	47.42259	-122.30538
Massey Creek		
MAS01	47.39601	-122.32166
MAS02	47.39443	-122.31611
MAS03	47.39428	-122.31599
McSorley Creek		
SOR01	47.37294	-122.32343
SOR02	47.37554	-122.31525
SOR03	47.37533	-122.31528

Datum = NAD83

Appendix B. Glossary and Acronyms

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 designated 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.

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.

Baseflow: Groundwater discharge.

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

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Synoptic surveys: Comprehensive water quality surveys designed to provide a water quality snapshot in a specific watershed. The surveys typically collect surface water grab samples under a variety of environmental conditions at a number of sites in the watershed. (Or "data collected over a short period of time.")

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

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

Cu	Copper
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management system
EPA	U.S. Environmental Protection Agency
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objectives
QA	Quality assurance
QC	Quality control

SOP	Standard operating procedure
TSS	Total suspended solids
WAC	Washington Administrative Code
Zn	Zinc