Quality Assurance Project Plan

High-resolution, Pore-water Sampling Near the Groundwater/Surface Water Interface

by
Charles F. Pitz
Licensed Geologist/Hydrogeologist

Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

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For more information contact:

Carol Norsen
Environmental Assessment Program
P.O. Box 47600
Olympia, WA 98504-7600
E-mail: CNOR461@ecy.wa.gov
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

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September 2008

Approved by:

Signature:	Date: September 2008
Charles F. Pitz, Project Manager, Principal Investigator, and EIM Data Engineer, Statewide Coordination Section, EAP	
Signature:	Date: September 2008
Martha Maggi, Unit Supervisor, Statewide Coordination Section, EAP	
Signature:	Date: September 2008
Will Kendra, Section Manager, Statewide Coordination Section, EAP	
Signature:	Date: September 2008
Stuart Magoon, Director, Manchester Environmental Laboratory, EAP	
Signature:	Date: September 2008
Bill Kammin, Ecology Quality Assurance Officer	

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

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Abstract

A variety of complex biogeochemical processes can be active immediately below the sediment surface in aquatic environments. These processes can cause significant changes in the water quality of groundwater discharging to a surface water system. These changes can often occur within the last several feet, or even inches, of the groundwater flow path.

The groundwater monitoring tools and methods currently used by the Washington State Department of Ecology (Ecology) Environmental Assessment Program (EAP) for groundwater/surface water interaction studies are not well-suited to accurately characterize changes in groundwater chemistry at this scale. Without accurate measurements of these changes, EAP estimates of groundwater discharge chemistry and pollutant loading to surface water can have a high degree of uncertainty. This uncertainty reduces our confidence in how accurately our models of groundwater/surface water exchange reflect the natural environment.

This project will focus on developing and testing a higher-resolution, pore-water sampling approach to improve description of groundwater discharge chemistry. These methods will in turn improve groundwater pollutant loading estimates developed for Total Maximum Daily Load (TMDL) numerical models. Test results and field procedures will be documented and evaluated, and if successful, applied in an ongoing TMDL groundwater study.

This test program is initially focused on improving methods for characterizing changes in nutrient concentration near the groundwater/surface water interface. The methods could also benefit evaluations of loading and attenuation for other groundwater-borne chemicals of interest entering surface water systems.

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, and a Standard Operating Procedure (SOP) for the method will be prepared.

Background

The federal Clean Water Act requires that a Total Maximum Daily Load (TMDL) be developed for all surface waterbodies failing to meet Washington State water quality standards. A TMDL is the estimated maximum amount of pollutant load that a waterbody can receive and still meet these standards. This estimate is sometimes also referred to as the waterbody's *loading capacity*. Defining a loading capacity can help to preserve and protect the beneficial uses of a waterbody.

One of the main objectives of a TMDL technical study is to conduct a quantitative assessment of current pollutant loading to the surface water system of interest, in order to compare that load to the system's loading capacity. Pollutant loading sources can include a combination of both point (e.g., discharge pipe) and nonpoint (e.g., stormwater runoff, groundwater discharge) inputs. During a TMDL study, each of these inputs needs to be quantified to determine how they individually contribute to the total pollutant load. If the current pollutant load exceeds a waterbody's loading capacity and prevents or inhibits beneficial use of the water, inputs from some or all of the pollutant sources need to be reduced.

Groundwater/Surface Water Exchange

A growing body of literature has highlighted the important role that nonpoint groundwater discharge[1] can play in sustaining, or degrading, surface water quality and flow (e.g., Winter et al., 1998; USEPA, 1991). As a result, EAP hydrogeologists have been asked to conduct a number of groundwater studies in support of TMDL loading assessments. For each of these studies, the hydrogeologist is tasked with quantifying groundwater's contribution to the surface water system of interest, both in terms of water volume and pollutant mass load. Ultimately, this information is incorporated into a numerical model to help describe the surface system's overall hydrodynamics and pollutant budget.

Estimates of unit area groundwater pollutant loading to a surface water system via advection are developed by:

$$F_M = Q*C \qquad (1)$$

where:

F_M = the mass flux of pollutant loaded to the surface waterbody by groundwater discharge [(mass/time)/unit area]
Q = the rate of groundwater discharge [(volume/time)/unit area]
C = the pollutant concentration of the groundwater discharge (mass/volume)

For EAP TMDL studies, flow field analysis using Darcy's Law is the standard approach for developing estimates of groundwater volume discharge (Q), while field sampling of the pore water located beneath (hydraulically upgradient of) the groundwater/surface water interface is the standard method for estimating pollutant discharge concentrations (C).

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[1] Also known as *seepage* or *inflow*.

EAP hydrogeologists typically complete the water quality sampling portion of a TMDL groundwater study by installing a network of small-diameter piezometers[2] into the streambed or lake-bed sediments approximately 1 to 2 meters below the interface. In settings where hydraulic head data indicate a groundwater discharge condition, samples of pore water are collected for chemical analysis through an open interval at the base of the piezometer. In addition to providing information about the water quality character of groundwater prior to its entry into a surface water system, piezometers are also used to test and monitor hydraulic conditions across the interface (e.g., hydraulic gradient and interface zone permeability) to support Darcian calculations.

Tracking Changes in Groundwater Chemistry Near the Point of Discharge

Research advances over the past decade have highlighted the remarkably dynamic nature of the interface zone or *membrane* between groundwater and surface water systems (Constanz, 2007; Winter et al., 1998; Ford, 2005; Bridge, 2005). A variety of complex biogeochemical processes (see Figure 1) can be active in this transition zone, including acid-base reactions, precipitation and dissolution of minerals, sorption and ion exchange, biodegradation, dissolution and exsolution of gases, and reduction-oxidation (redox) reactions. These processes can create strong vertical solute concentration gradients over short distances and significantly influence the chemical character of the groundwater that finally discharges to a surface water system (USEPA, 2000a; Ford, 2005; Laskov et al., 2007).

In many cases, dissolved chemical concentrations measured a short distance upgradient of the interface are reduced or *attenuated* as groundwater approaches the point of discharge to surface water, potentially by an order of magnitude or more (Ford, 2005; Duff et al., 1998; Charette and Sholkovitz, 2002). These attenuation reactions can have a significant bearing on the estimated total groundwater-related chemical load to a surface system, even at a watershed scale (Harvey and Fuller, 1998; Angier and McCarty, 2008). Two key nutrients for Washington State TMDL studies (phosphorus and nitrogen) are particularly subject to these attenuation reactions (Charette and Sholkovitz, 2002; Chambers and Odum, 1990; Cox et al., 2005; Maleki et al., 2004; Fisher and Reddy, 2001)[3].

While there are a number of factors that can influence the thickness of the transition zone between *normal* aquifer conditions and *discharge* conditions, an increasing body of research indicates that the majority of groundwater solute concentration changes occur within 50 cm of the sediment surface (Chambers and Odum, 1990; Beck et al., 2007; Berg and McGlathery, 2001; Dean et al., 1999; Duff et al., 1998, Martin et al., 2003; Ford, 2005). Most of the water quality samples collected using traditional piezometers are taken below (hydraulically upgradient of) this depth. Therefore, the groundwater pollutant loading estimates provided to the surface water modeler by EAP hydrogeologists have had very high levels of uncertainty (usually presented as upper-bound values). This is especially true for loading estimates for highly

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[2] A piezometer is essentially a small diameter well.

[3] Denitrification reactions at the groundwater/surface water interface could also be of significant interest in the development of nutrient loading estimates for Puget Sound (Pitz, 1999; Simonds et al., 2008).

reactive, redox-sensitive pollutants such as phosphorus, a common TMDL parameter of interest (Chambers and Odum, 1990; Charette and Sholkovitz, 2002; Pitz, 2005).

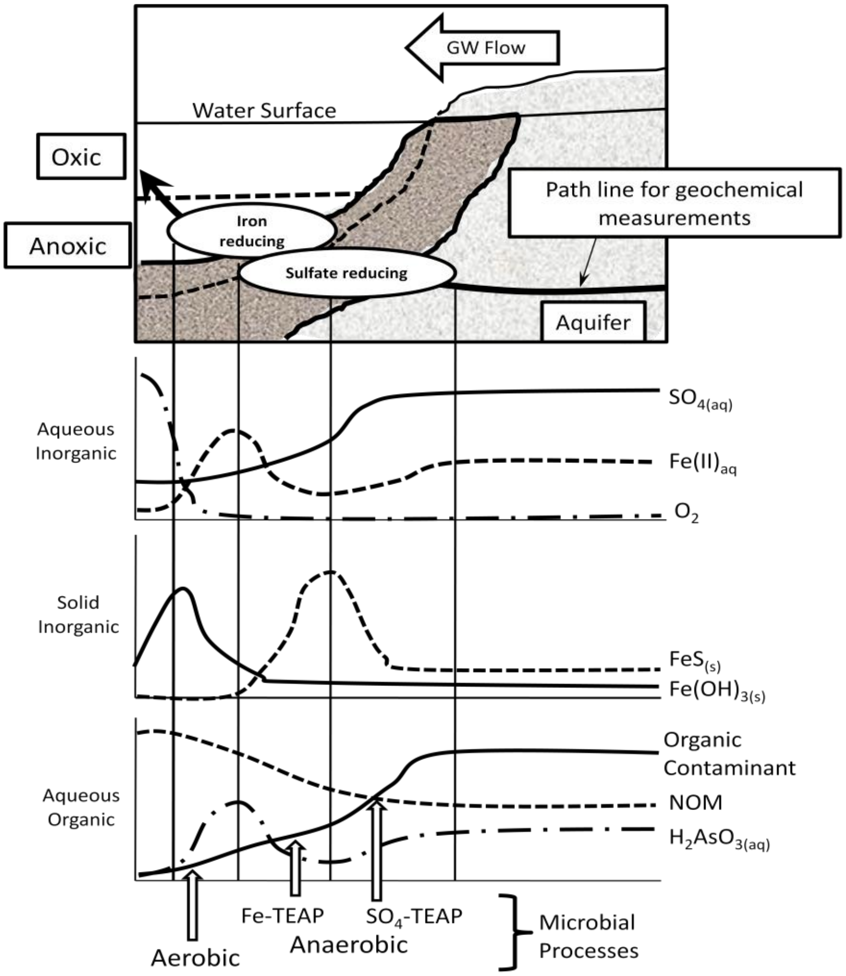

Figure 1. Conceptual diagram showing type chemical component profiles across the groundwater/surface water interface. NOM = natural organic matter, TEAP = terminal electron acceptor process. (Figure from Ford, 2005).

Even small changes in the estimated discharge concentration can have a significant influence on the final groundwater loading estimate the hydrogeologist provides the surface water modeler (Equation 1). Therefore, it is critical to try to collect water quality samples that are as representative as possible of the final discharge concentration. New, higher-resolution field monitoring tools and methods could improve description of spatial changes in solute concentration immediately below the groundwater/surface water interface. These tools and methods would help to reduce uncertainty and improve the overall accuracy of the TMDL loading assessments and numerical modeling efforts conducted by EAP. These tools and procedures also have potential for application in a variety of other EAP studies involving investigation of groundwater discharge to surface water (e.g., mapping toxic or nutrient groundwater plume entry/attenuation to Puget Sound).

Project Description

This project will focus on researching and testing techniques and tools for high-resolution, pore-water profiling of nutrient concentration gradients immediately below the groundwater/ surface water interface. The ultimate goal of the project is to improve current EAP methods for estimating nutrient loading from aquifer systems to surface waterbodies.

The objectives of the study include:

- Research device designs and methods for high-resolution, pore-water sampling near the groundwater/surface water interface. Identify approaches that are low-cost, time efficient, and field robust. Select a preferred approach for field testing; modify as necessary to suit the needs of EAP field studies.
- Construct or purchase sampling equipment for field testing the selected approach.
- Install and sample test devices in an appropriate field setting. Evaluate, refine, and document field operating procedures.
- Assuming a successful trial outcome, deploy and use the new methods in an active EAP TMDL loading assessment project where groundwater nutrient discharge is of concern.

A review of the variety of published approaches used for interface zone sampling was completed in support of the development of this Quality Assurance Project Plan. The approaches surveyed included permeable membrane diffusion samplers, pore-water extractors, and in-situ chambers and probes. After evaluation of existing literature, and consultation with experts in the field, an ultra-low-flow sampling process using the M.H.E., Inc. *PushPoint* sampling device was selected for further testing. The specific methods and equipment proposed for evaluation (described in detail later in this plan) are a modification of approaches developed and described by Duff et al. (1998), Zimmerman et al. (2005), Ford (2005), Henry (2003), and USEPA (2000b).

Trial testing for the selected sampling approach is proposed for late summer or early fall 2008, at a location in Lake Whatcom, in Whatcom County, Washington. Previous piezometer-based sampling at the proposed site (LWGW-09) indicated a highly elevated dissolved phosphorus concentration approximately 1.5 meters below the groundwater/surface water interface (Pitz, 2005). Water quality measurements from the original piezometer consistently exhibited a positive vertical hydraulic gradient (indicating a groundwater discharge condition), and sub-oxic to anoxic pore-water conditions [<1-2 milligram/liter (mg/L) dissolved oxygen, elevated dissolved iron]. Sediment character was predominantly poorly-graded sand with silt, suggesting moderate permeability and groundwater velocity conditions.

Combined, these conditions suggest that groundwater discharge at this site may undergo significant redox-driven attenuation of phosphorus (likely by sorption to iron hydroxides) in the final tens of centimeters of the flow path, just prior to entry to the lake. This site is well suited for testing procedures for high-resolution profile sampling to confirm this assumption. Information indicating the possibility of significant phosphorus loading attenuation potential at the groundwater/surface water interface could be of benefit to the Lake Whatcom TMDL modeling effort (Hood, 2008).

Analysis of profile samples will focus on:

- Key field parameters: dissolved oxygen (DO) and ferrous iron (Fe^{2+}).
- Laboratory analysis for: orthophosphate (OP), total dissolved phosphorus (TDP), and nitrogen (ammonia as N)[4].

Chloride will also be analyzed for use as a conservative tracer.

Assuming a successful trial test of the sampling approach, the sampling methods will be applied on a project-scale to a nutrient-based groundwater/surface water loading study on the Touchet River in Walla Walla County, Washington. This study, focused in the vicinity of the City of Waitsburg Wastewater Treatment Plant, is scheduled for field sampling in the summer of 2009. The results of that work will be reported separately from the trial testing described in this Quality Assurance Project Plan.

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[4] Previous samples at this location displayed negligible nitrite+nitrate-N concentrations.

Organization and Schedule

The personnel involved in this project are listed in Table 1. A proposed project schedule is presented in Table 2.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Charles F. Pitz GFF Unit SCS (360) 407-6775	Project Manager/ Principal Investigator/ EIM Data Engineer	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.
Niki Thane Western Washington Univ. Dept. of Geology (graduate student) (360)734-9052	Field Assistant	Helps collect samples and records field information.
Martha Maggi GFF Unit SCS (360) 407-6453	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra SCS (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.
Stuart Magoon Manchester Environmental Laboratory (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

GFF – Groundwater/Forests & Fish
SCS – Statewide Coordination Section
EAP – Environmental Assessment Program
EIM – Environmental Information Management system
QAPP – Quality Assurance Project Plan

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

Field and laboratory work	
Field work completed	October 2008
Laboratory analyses completed	November 2008
Environmental Information System (EIM) system	
EIM data engineer	Charles F. Pitz
EIM user study ID	CHPI003
EIM study name	High-resolution gw/sw interaction sampling
Data due in EIM	April 2009
Groundwater report (Technical Memo/SOP)	
Project Tracker code	09-146
Author lead	Charles F. Pitz
Schedule	
Draft due to supervisor	February 2009
Draft due to client/peer reviewer	February 2009
Final report due on web	April 2009

Quality Objectives

The primary goal of this project is to develop and refine an efficient, standardized method for high-resolution profile sampling of pore water in the vicinity of the groundwater/surface water interface. To be of use in future EAP studies, the new method must provide data that are representative of in-situ pore-water conditions. In order to distinguish variations in pore-water chemistry due to natural environmental heterogeneity from variations caused by measurement or procedural error, quality criteria for project analytical methodology need to be established. Providing clear criteria for data quality, stated as measurement quality objectives (MQOs), helps assess potential sources of error (e.g., laboratory and sampling error) when evaluating precision and bias for the proposed method.

Table 3 and 4 present the MQOs that will be used when assessing project data quality. Manchester Environmental Laboratory (MEL) is expected to meet quality control requirements for the laboratory methods selected for the project.

Table 3. Field Analyte Measurement Quality Objectives.

Analyte	Accuracy	Required Reporting Limit	Field Replicate Precision
pH	±0.15 s.u.	n/a	<10% RPD
SC	±10 µS/cm	n/a	<10% RPD
ORP	±20 mV	n/a	<20% RPD
DO (probe)	±0.2 mg/L	1 mg/L	<20% RPD
DO (chemical)	~±0.5 mg/L @1-12 mg/L ~±0.05 mg/L @ 0.025–1 mg/L	25 µg/L	<20% RPD
Ferrous iron (Fe^{2+})	~ ±5 µg/L @ 0-1 mg/L ~ ±0.5 mg/L @ 1-10 mg/L	50 µg/L	<20% RPD

See the Appendix for acronym definitions.

Table 4. Laboratory Analyte Measurement Quality Objectives.

Analyte	LCS % Recovery	Lab Duplicate Precision RPD	Matrix Spikes %Recovery	Matrix Spike RPD	Required Reporting Limit*	Field Replicate Precision
OP	80-120	20	75-125	20	3 µg/L	<15% RSD
TDP	80-120	20	75-125	20	5 µg/L	<15% RSD
Ammonia-N	80-120	20	75-125	20	10 µg/L	<10% RSD
Chloride	90-110	20	75-125	20	0.1 mg/L	<10% RSD

* The stated reporting limit is for undiluted water samples. In cases where the sample volume submitted to the laboratory is too small for analysis by the method requested, a dilution may be performed by the laboratory *at the discretion of the project manager*. It is recognized that in such cases, the reporting limit will increase by the factor of dilution.

See the Appendix for acronym definitions.

Experimental Design

Based on the findings of previous investigators, high-resolution profile sampling will be focused during this project in the uppermost 50 centimeters (cm) of trial-site sediments. Dependent on field conditions, profile pore-water samples will be collected and compared from the following depth intervals: 5 cm, 10 cm, 15 cm, 25 cm, and 50 cm. Sample retrieval will be conducted using ultra-low-flow techniques to avoid inducing hydraulic or concentration gradient changes that could lead to cross-contamination of sample intervals.

The original 1.5-meter-deep piezometer installed at the test location during the 2002-2003 Lake Whatcom TMDL groundwater study (LWGW-09) was left in place at the end of the study. Depending on current condition, this piezometer will be re-sampled for comparison purposes to the shallower intervals, using the procedures outlined in Pitz (2002).

A sample of overlying surface water will also be collected as a quality control measure of *cross-pumping.*[5]

Since the primary objective of the current project is to refine spatial sampling methods (versus temporal concentration variations), only one sampling event will be conducted.

The success of the proposed methods will ultimately be judged by the ability to produce:

- An adequate sample volume for chemical analysis.
- A water sample free of surface water cross-contamination.
- Quality control blanks free of significant contamination.
- Duplicate sample results within acceptable quality objective criteria.
- Water samples in a time efficient and field robust manner.

If the project data results indicate the proposed methods are not capable of meeting the above criteria, the equipment or field techniques will be revised, in consultation with topic experts, and re-tested.

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[5] Cross-pumping occurs when surface water is drawn into the pore-water sampling port due to excessive pumping rates and/or vertical leakage through annular space between the sampling device and the sediments.

Testing and Sampling Procedures

Annular Leakage Test Procedures

Prior to collecting samples for laboratory analysis, the PushPoint sampling device will be tested at a first location using the measurement system illustrated in Figure 2. This system will be used to confirm the ability of the device to collect a pore-water sample free of surface water contamination due to annular leakage. Previous studies (Pitz, 2003; Pitz, 2005; Pitz et al., 2005; Duff et al., 1998) have demonstrated that field water quality measurements for pore-water samples collected from small diameter piezometers consistently display a distinct profile from those measured in overlying surface water, as long as the two systems are not hydraulically connected by leakage through the annular space adjacent to the sampler casing.

To test the sampling system for annular leakage:

- Drive the PushPoint device to the desired sediment depth position.
- Measure and compare the relative pore-water potentiometric head and surface water stage to establish the vertical hydraulic gradient between groundwater and surface water. Water levels will be measured and compared using a stilling tube and metric scale.
- Collect field measurements of pH, specific conductance (SC), oxidation reduction potential (ORP), and DO by electrode probe from surface water immediately adjacent to the entry point of the sampler. Measure in a closed-atmosphere chamber or *flow block* to avoid bias from atmospheric exposure.
- Connect the measurement system to the sampler, and retrieve pore water into the chamber using low-flow pumping techniques (within the limits of a standard peristaltic pump). Record parameter measurements at five-minute intervals until equilibration (i.e. all introduced surface water has been purged from the system). Equilibration will be confirmed by two consecutive measurement sets less than 10% apart in value. Compare end-of-purge measurements to surface water conditions to confirm hydraulic isolation[6]. If the data comparison indicates annular leakage, take additional measures to seal the annular space at the sediment surface (e.g., by burying the rim of the stabilizing plate in the top sediments). Annular leakage tests will be conducted at 5 cm, 10 cm, and 25 cm depth intervals.

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[6] Maintenance of a positive (upward) hydraulic head difference between the PushPoint device and surface water is an additional indicator of hydraulic isolation.

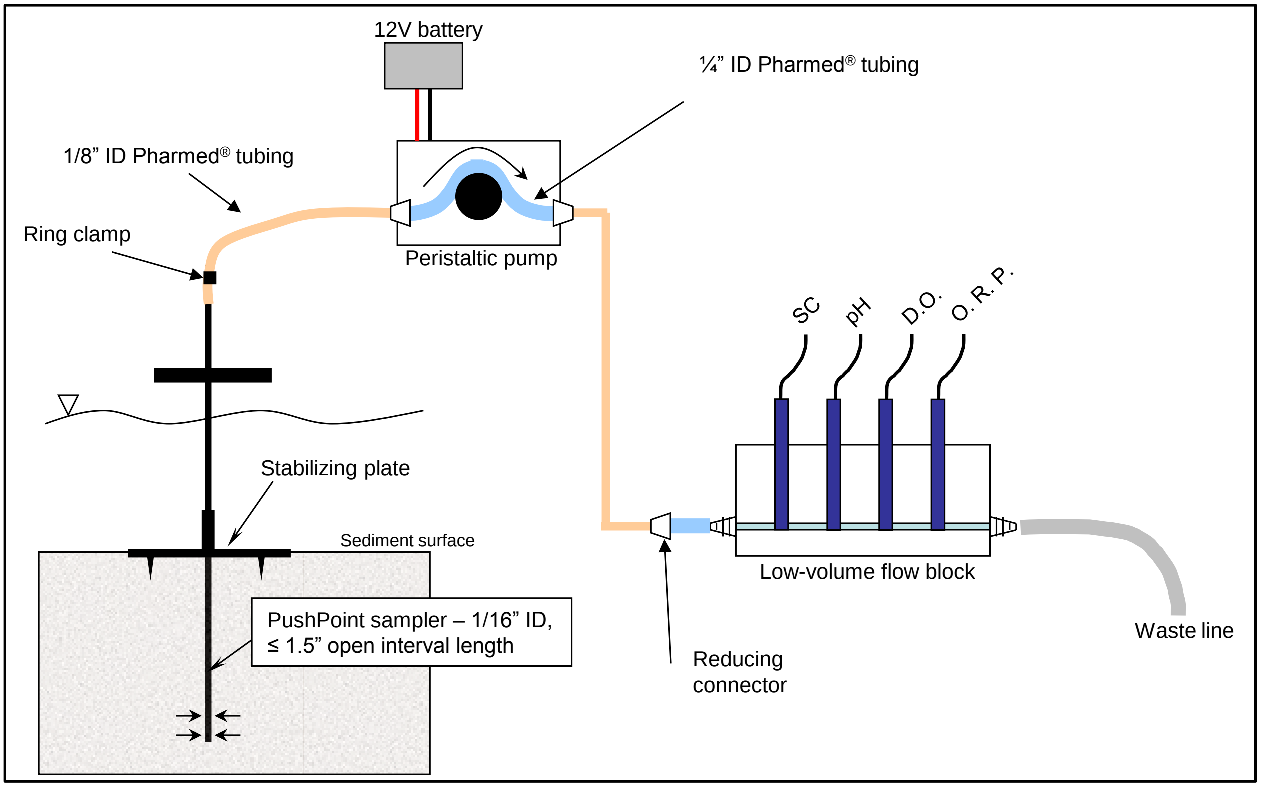

Figure 2. Schematic of proposed system for leakage testing.

Sampling Procedures

A schematic of the proposed sampling system is presented in Figure 3. The sampling approach follows methods modified from Duff et al. (1998), Zimmerman et al. (2005), and Henry (2003).

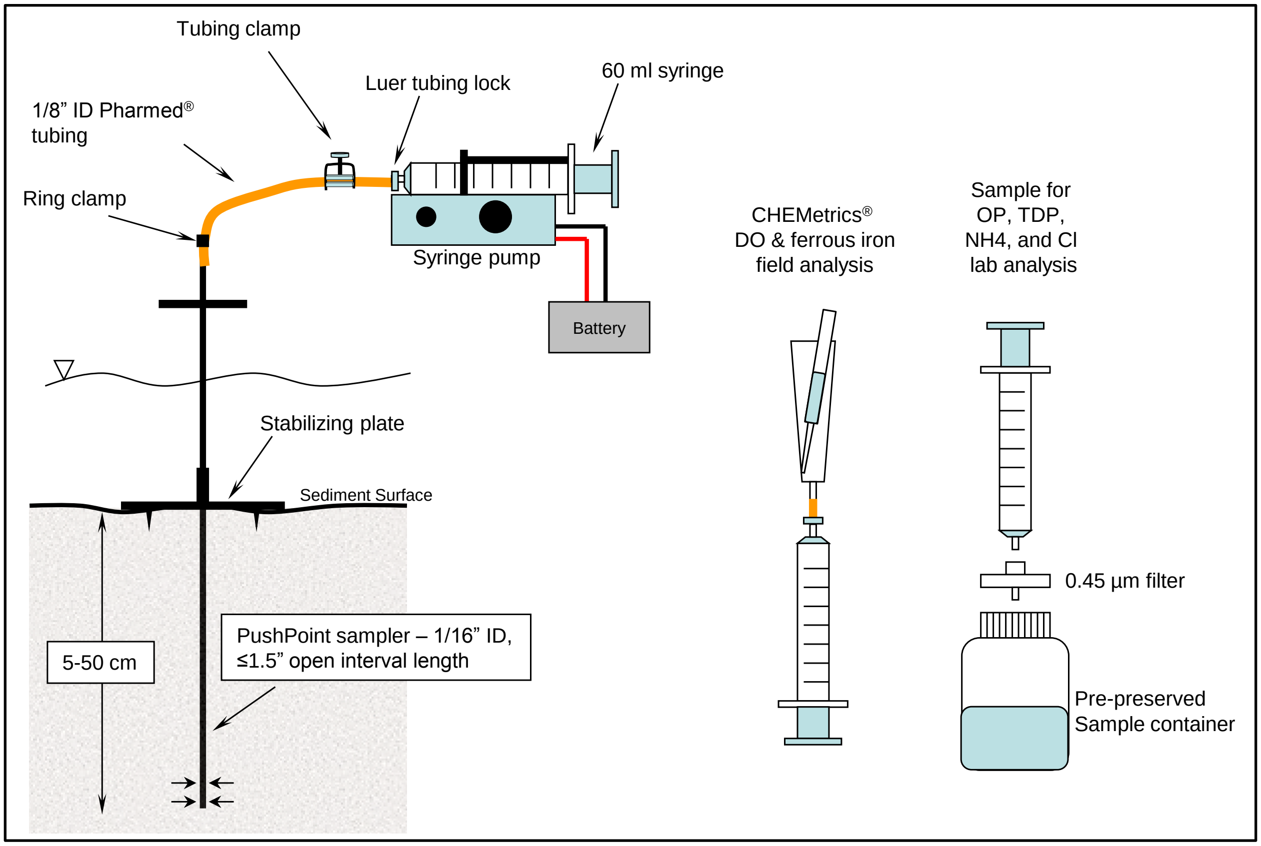

Figure 3. Schematic of proposed system for high-resolution, pore-water sampling.

Pore-water samples will be collected using the following general procedures, to be refined in the field during testing:

- At a new location, drive the PushPoint sampler to the appropriate depth interval (5, 10, 15, 25, and 50 cm).
- Measure and compare the relative pore-water potentiometric head and surface water stage to establish the vertical hydraulic gradient between groundwater and surface water. Water levels will be measured and compared using a stilling tube and metric scale.
- Measure field parameters (DO and ferrous iron) for surface water located adjacent to the entry point of the sampler using CHEMetrics® field analysis kits.
- Purge and discard approximately 1.2 times the interior volume of the sampling system using ultra low-flow pumping techniques (≤ 2.5 ml/min, by programmable syringe pump) to remove surface water potentially introduced during device installation.

- After purge, continue ultra low-flow pumping to collect a pore-water sample for analysis of redox-sensitive field parameters (DO and ferrous iron).
- After analysis of field parameters, collect additional sample volume for laboratory analysis. Field filter all samples through a pre-soaked 0.45 µm cartridge filter directly into the appropriate container.
- Re-measure the potentiometric head to confirm maintenance of positive (upward) gradient.
- Withdraw the sampling device, re-install to the next depth interval (a minimum horizontal distance of 10 cm from the previous sampling location), and repeat sampling procedure.

Surface water samples will be collected into a syringe for measurement or filtration using clean tubing. The sample tubing will be positioned within 10 centimeters of the entry point of the sampler into the sediments.

All water samples for laboratory analysis will be collected into clean laboratory-supplied containers. Table 5 presents the proposed container type for each analyte, as well as sample handling, preservation, and holding time information.

Table 5. Sample and Container Volume, Handling, Preservation, and Holding Time Requirements.

Analyte	Expected sample volume	Container type	Container volume	Sample handling	Preservation	Holding time
OP	~20 ml	Amber w/m poly	125 ml	Filter @ 0.45 micron	Cool to <4^{o}C	48 hrs.
TDP	~20 ml	w/m clear Nalgene (pre-acidified)	125 ml(A)	Filter @ 0.45 micron	Adjust pH <2 w/H_2SO_4 and cool to <4^{o}C	28 days
Ammonia-N	~20 ml	w/m clear Nalgene (pre-acidified)	125 ml(A)	Filter @ 0.45 micron	Adjust pH <2 w/H_2SO_4 and cool to <4^{o}C	28 days
Chloride	~20 ml	w/m poly (hardness bottle)	60 ml	Filter @ 0.45 micron	Cool to <4^{o}C	28 days

(A) TDP and ammonia-N samples will be collected in a common 125-ml nutrients bottle.

High-resolution, pore-water profile sampling requires very low sample withdrawal rates from the sediment column in order to avoid changing natural hydraulic and chemical gradients. Combined with the small volume capacity of the sampling equipment, and the time required to complete sample collection, the sample volume available for laboratory analysis will be smaller than normally preferred by MEL.

Table 5 indicates the expected volume of sample available for each laboratory analyte for each sample. If the sample volume submitted to the laboratory is inadequate to run the desired method, the sample may be diluted with reagent-grade water *at the discretion of the project manager, in consultation with the MEL analyst.* Laboratory reporting limits for diluted samples will increase by the factor of dilution required to reach the necessary sample volume.

Hydraulic Conductivity Test Procedures

To quantify the permeability character of the sampled sediments, a constant-head injection test (CHIT) will also be performed at ~25 cm and ~50 cm below the sediment surface at the test location. The CHIT will be run after water quality sampling is complete to avoid cross contamination of pore-water chemical conditions. Detailed procedures for running the CHIT are described in Pitz (2006).

Measurement Procedures

A combination of field-based and laboratory-based analytical techniques will be used during the project to quantify the chemical status of the samples. Table 6 presents the expected analyte concentration ranges for the project water samples (from Pitz, 2005).

Table 6. Expected ranges for analytes of interest.

Analyte	Expected Range
pH	5.5 – 7.5 s.u.
SC	325- 375 µS/cm
ORP	-400 - +800 mV
DO	Method Reporting Limit – 2 mg/L
OP	Method Reporting Limit – 1 mg/L
TDP	Method Reporting Limit – 3 mg/L
Ammonia-N	Method Reporting Limit – 2 mg/L
Chloride	Method Reporting Limit – 15 mg/L

See the Appendix for acronym definitions.

A summary of the analytical methods for both field and laboratory parameters is presented in Table 7. Previous groundwater studies have indicated that, relative to natural spatial and temporal heterogeneity, the precision and accuracy routinely obtained by the methods selected are considered adequate for the goals of the project. Field personnel will follow standardized procedures for collecting accurate field measurements, as well as handling, preserving, and storing samples intended for delivery to MEL.

The total laboratory costs for this project are estimated at $944. Costs include a 50% discount for Manchester Laboratory services. Itemized analytical costs are shown in Table 8.

Table 7. Summary of Project Measurement Methods.

Analyte(A)	Equipment Type or Test Method(B)(C)	Reporting Limit(D)
Field		
pH	Sentix® 41-3 electrode probe(E) - EPA Method 150.1	0.1 SU
SC	Tetracon® 325 electrode pair probe(E) - EPA Method 120.1	1 µS/cm
ORP	Sentix® electrode probe(E) – SM2580-B	±2000mV measurement range; 1mV resolution
DO	CHEMetrics® Rhodazine D/Indigo Carmine colorimetric – ASTM D888-87, ASTM D 5543-94; CellOx 325 electrochemical probe (O_2 permeable membrane) – EPA Method 360.1	25 µg/L
Ferrous Iron	CHEMetrics® Phenanthroline colorimetric SM3500-Fe B	50 µg/L
Laboratory		
OP	SM 4500-P G (colorimetric)	3 µg/L
TDP	SM 4500-P F (colorimetric)	5 µg/L
Ammonia-N	SM 4500-NH3 H (colorimetric)	10 µg/L
Chloride	EPA Method 300.0/SM 4110C	0.1 mg/L

(A) All samples will be field-filtered water matrix.
(B) SM – Standard Method (APHA, AWWA, and WEF, 1998).
(C) ASTM – American Society for Testing and Materials Method.
(D) The reporting limit is for an undiluted sample. The reporting limit increases by the factor of dilution in cases where a sample requires dilution.
(E) Probe to be used with a WTW multi-line 197i meter.
TBD – to be determined

Table 8. Project Laboratory Costs.

Parameter	Total Number of Expected Samples	Analysis Cost per Sample	Subtotal Cost
OP	16	$15	$240
TDP	16	$18	$288
Ammonia-N	16	$13	$208
Chloride	16	$13	$208
		Total Cost:	$944

Quality Control Procedures

Field

To assist in evaluating the variability introduced into the sample results by a combination of field and laboratory influences, three field split replicates (from the 10cm, 25cm, and 50cm depth intervals) will be collected and submitted to the laboratory as blind samples. Replicate samples will be analyzed for the target laboratory parameters: OP, TDP, ammonia-N, and chloride.

To determine the bias introduced into the analytical results by sample-contact equipment and field handling, three replicate field equipment blanks will be collected at the beginning of the project. Equipment blanks will be collected by pumping reagent-grade de-ionized (DI) water through the sampling system, using new parts in all contact portions of the system (e.g., tubing, fittings, filters, and sample containers). Equipment blanks will be submitted to the laboratory as blind samples, and will be analyzed for all target parameters.

To determine the effectiveness of field equipment decontamination procedures in preventing cross-contamination between sample sets, three decontamination blanks will be collected and submitted to the laboratory for analysis (as blind samples). Each decontamination blank will be collected between real sampling intervals by pumping reagent-grade DI water through the sampling system after the equipment has been field cleaned. Sample contact equipment will be decontaminated between sample intervals by triple rinsing using a pressure sprayer and DI water. Decontamination blanks will be analyzed for all target parameters.

Additional quality control measures to minimize the risk of contamination of low-volume samples include use of clean sampling gloves for each sample set, use of small volume sample capture equipment, thorough equipment decontamination between sets, and pre-rinsing of sample contact equipment with sample water prior to collection to a container.

All field meters will be calibrated in accordance with the manufacturer’s instructions at the start of each sampling day.

Laboratory

Routine laboratory quality control procedures will be used to estimate the accuracy, precision, and bias introduced by laboratory procedures and will be reported to the project lead for data analysis (MEL, 2005). Manchester Laboratory’s quality control samples and procedures are discussed in detail in the Quality Assurance Manual, Manchester Environmental Laboratory (MEL, 2006). Laboratory duplicate samples will be used to independently assess the precision of the MEL analytical methods, separate from the influence of environmental and sampling variability.

Data Management Procedures

Field-based measurement data and observations will be collected in field note books. Before leaving site locations, data will be checked for legibility and completeness. Field notes will be stored with other project files. Pertinent field data will be transferred from field notes to electronic format as appropriate, using Microsoft Office Excel spreadsheet or Access database programs.

Analytical data from MEL will be stored in electronic format in the MEL data management system (LIMS). After the data are verified, they will be summarized in case narratives, and provided to the project manager.

Field and laboratory data for the project will be entered into Ecology's EIM system. Laboratory data will be downloaded directly into EIM from the MEL data management system (LIMS). Data entry into EIM is conducted using established data entry business rules. The EIM data will be reviewed by the project manager, staff entering the data (if different than the project manager), and an independent reviewer.

Audits and Reports

Manchester Laboratory participates in performance and system audits of their routine procedures. Reported results of these audits are available on request.

A technical memo or short-form technical report will be prepared documenting the study procedures, findings, and recommendations. In addition, a standard operating procedure will be developed for the field methods evaluated during this study. Drafts of these documents are expected to be available for review by February 2009; final versions are expected by April 2009.

Data Verification

Data Verification

Data verification is a review process to assess the quality and completeness of analytical datasets. Verification of laboratory data is normally performed by a MEL unit supervisor or an analyst experienced with the analytical method(s) of interest. Data will be examined for errors, omissions, and compliance with quality control acceptance criteria; data qualifiers will be assigned where necessary. Findings of the data verification effort will be documented in a case narrative, prepared by the appropriate MEL staff member. The case narrative will be forwarded to the project manager for review and acceptance.

Field quality control procedures, including duplicate measurements and review of field note completeness and accuracy, will support verification of field-based analytical measurements.

Data Usability Assessment

The data usability review involves a detailed evaluation of the project data package using professional judgment to determine if the project measurement quality objectives have been met. The project manager will compare verified data (both field and laboratory) against established standards for acceptable precision and bias, by evaluation of MEL case narratives and blind quality control data results. As appropriate, the project manager will assign additional data qualifiers where necessary.

The project manager will evaluate all data generated during the study to determine if the information is of acceptable quality, is complete, is properly qualified where appropriate, and can be used for the project objectives. The final technical memo for the project will discuss data quality, usability, and limitations. Documentation of standard operating procedures will identify steps to help ensure data quality during future application of the methods tested.

References

Angier, J.T., and McCarty, G.W., 2008. Variations in Base-flow Nitrate Flux in a First-order Stream and Riparian Zone, Journal of the American Water Resources Association, Vol. 44, No. 2, p. 367- 380.

APHA, AWWA, and WEF, 1998. Standard Methods for the Examination of Water and Wastewater 20th Edition. American Public Health Association, Washington, D.C.

Beck, M., Dellwig, O., Kolditz, K., Freund, H., Liebezeit, G., Schnetger, B., and Brumsack, H., 2007. In-situ pore water sampling in deep intertidal flat sediments, Limnology and Oceanography: Methods, p. 136-144.

Berg, P. and McGlathery, K.J., 2001. A high-resolution pore water sampler for sandy sediments, Limnology and Oceanography, v. 46(1), p. 203-210.

Bridge, J.W., 2005. High resolution in-situ monitoring of hyporheic zone biogeochemistry, United Kingdom Environment Agency Science Report SC030155/SR3, 51p. http://publications.environment-agency.gov.uk/pdf/SCHO0605BJCO-e-e.pdf

Chambers, R.M. and Odum, W.E., 1990. Porewater oxidation, dissolved phosphate and the iron curtain – Iron-phosphorus relations in tidal freshwater marshes, Biogeochemistry, v. 10, p. 37-52.

Charette, M.A. and Sholkovitz, E.R., 2002. Oxidative precipitation of groundwater derived ferrous iron in the subterranean estuary of a coastal bay, Geophysical Research Letters, v. 29, n. 10, p. 85-1 to 85-4.

Constanz, J., 2007. The Streambed as a Dynamic Membrane in the Watershed, Abstract, Eos Transactions American Geophysical Union, 88(52), Fall Meeting Supplement.

Cox, S.E., Simonds, F.W., Huffman, R.L., Doremus, Llyn, Defawe, R.M., 2005. Ground water/ surface water interactions and quality of discharging ground-water in streams of the Lower Nooksack River Basin, Whatcom County, Washington: U.S. Geological Survey Scientific Investigations Report 2005-5255, 46 p. http://pubs.water.usgs.gov/sir2005-5255/

Dean, S. M., Lendvay, J. M., Barcelona, M. J., Adriaens, P., and Katopodes, N.D., 1999. Installing Multilevel Sampling Arrays to Monitor Ground Water and Contaminant Discharge to a Surface Water Body, Ground Water Monitoring and Remediation, v. 19, no. 4, p. 90-96.

Duff, J. H., Murphy, F., Fuller, C. C., Triska, F. J., Harvey, J. W., and Jackman, A. P., 1998. A mini drivepoint sampler for measuring pore water solute concentrations in the hyporheic zone of sand-bottom streams, Limnology and Oceanography, v. 43(6), p. 1378-1383.

Fisher, M.M., and Reddy, K.R., 2001. Phosphorus Flux from Wetland Soils Affected by Long-Term Nutrient Loading, Journal of Environmental Quality, V. 30, p. 261-271.

Ford, R.G., 2005. The Impact of Ground-water/Surface-water Interactions on Contaminant Transport with Application to an Arsenic Contaminated Site; U.S. EPA Environmental Research Brief, National Risk Management Research Laboratory, Ada, OK, EPA 600-S-05-002, 22 p. www.epa.gov/ada/download/briefs/epa_600_s05_002.pdf

Harvey, J.W., and Fuller, C.C., 1998. Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, Water Resources Research, V. 34, No. 4, p. 623-636.

Henry, M., 2003. PushPoint Sampler Operators Manual and Applications Guide, v. 2.01, M.H.E. Products, Inc. www.mheproducts.com/MHE-instructions-ver-2.01.doc

Hood, S., 2008. Personal communication, Washington State Department of Ecology, Water Quality Program, Bellingham, WA.

Laskov, C., Herzog, C., Lewandowski, J., and Hupfer, M., 2007. Miniaturized photometrical methods for the rapid analysis of phosphate, ammonium, ferrous iron, and sulfate in pore water of fresh sediments, Limnology and Oceanography: Methods 4, p. 63-71.

Maleki, L.M, White, J.R., and Reddy, K.R., 2004. Nitrogen and Phosphorus Flux Rates from Sediment in the Lower St. Johns River Estuary, Journal of Environmental Quality, v. 33, p. 1545-1555.

Martin, J. B., Hartl, K. M., Corbett, D. R., Swarzenski, P. W., and Cable, J. E., 2003. A Multi-level Pore-water Sampler for Permeable Sediments, Journal of Sedimentary Research, v. 73, no. 1, p. 128-132.

MEL, 2005. Manchester Environmental Laboratory Lab Users Manual, Eighth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2006. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Microsoft, 2007. Microsoft Office Professional Plus 2007, Version 12. Microsoft Corporation.

Pitz, C.F., 1999. Estimates of Nitrate-N Loading to South Puget Sound by Groundwater Discharge, Washington State Department of Ecology, Olympia, WA. Publication No. 99-348, 17 p. www.ecy.wa.gov/biblio/99348.html

Pitz, C.F., 2002. Quality Assurance Project Plan: Characterization of Groundwater Discharge to Lake Whatcom, Washington State Department of Ecology, Olympia, WA. Publication No. 02-03-082, 21 p. www.ecy.wa.gov/biblio/0203082.html

Pitz, C.F., 2003. Moses Lake Total Maximum Daily Load Groundwater Study, Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-005, 72 p. + apps. www.ecy.wa.gov/biblio/0303005.html

Pitz, C.F., 2005. Lake Whatcom Total Maximum Daily Load Groundwater Study, Washington State Department of Ecology, Olympia, WA. Publication No. 05-03-001, 55 p. + apps. www.ecy.wa.gov/biblio/0503001.html

Pitz, C.F., 2006. An Evaluation of a Piezometer-based Constant-Head Injection Test for use in Groundwater/Surface Water Interaction Studies, Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-042, 18 p. + app. www.ecy.wa.gov/biblio/0603042.html

Pitz, C.F., Sinclair, K., and Oestreich, A.J., 2005. Hydrology and Quality of Groundwater in the Centralia-Chehalis Area Surficial Aquifer, Washington State Department of Ecology, Olympia, WA. Publication No. 05-03-040, 104 p. www.ecy.wa.gov/biblio/0503040.html

Simonds, F.W., Swarzenski, P.W., Rosenberry, D.O., Reich, C.D., and Paulson, A.J., 2008. Estimates of Nutrient Loading by Ground-Water Discharge into the Lynch Cove Area of Hood Canal, Washington, U.S. Geological Survey Scientific Investigations Report 2008-5078, 66 p. http://pubs.usgs.gov/sir/2008/5078/

US.EPA, 1991. A Review of Methods for Assessing Nonpoint Source Contaminated Ground-Water Discharge to Surface Water, EPA/570/9-91/010. U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA, 2000a. Proceedings of the Ground-Water/Surface-Water Interactions Workshop, EPA/542/R-00/007, Parts 1-3. U.S. Environmental Protection Agency.
www.epa.gov/tio/download/remed/gwsw/gwsw_part1.pdf
www.epa.gov/tio/tsp/download/gwsw/gwsw_part2.pdf
www.epa.gov/tio/tsp/download/gwsw/gwsw_part3.pdf

U.S. EPA, 2000b. Workshop on Monitoring Oxidation-Reduction Processes for Ground-Water Restoration, Workshop Summary, Dallas, Texas, April 25-27, 2000, EPA/600/R-02/002. U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Cincinnati, OH.
www.epa.gov/ada/download/reports/epa_600_r02_002.pdf

Winter, T.C., Harvey, J.W., Franke, O.L., and Alley, W.M., 1998. Ground Water and Surface Water – A Single Resource, U.S. Geological Survey Circular 1139, 79 p.
http://pubs.usgs.gov/circ/circ1139/

Zimmerman, M.J., Massey, A.J., and Campo, K.W., 2005. Pushpoint Sampling for Defining Spatial and Temporal Variations in Contaminant Concentrations in Sediment Pore Water near the Ground-Water/Surface-Water Interface, U.S. Geological Survey Scientific Investigations Report 2005-5036, 75 p. http://pubs.usgs.gov/sir/2005/5036/pdf/sir2005_5036.pdf

Appendix: Glossary, Acronyms, and Abbreviations

Glossary

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.

Groundwater discharge: The movement of groundwater from the subsurface to the surface by advective flow.

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

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but 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 National Pollutant Discharge Elimination System 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.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

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

Pore water: The water filling the spaces between grains of sediment.

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.

Upgradient: In hydrology, an *upgradient* location is one that exhibits a larger hydraulic head in comparison to a *downgradient* location. Water flows from areas of high hydraulic head to areas of low hydraulic head. Hydraulic head is the total pressure exerted by a water mass at any given point. Total hydraulic head is the sum of elevation head, pressure head, and velocity head.

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

EAP	Environmental Assessment Program (Ecology)
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database (Ecology)
LCS	Laboratory control samples
MQO	Measurement quality objectives
MEL	Manchester Environmental Laboratory (Ecology)
OP	Orthophosphate
ORP	Oxidation reduction potential
RPD	Relative percent difference
RSD	Relative standard deviation
SC	Specific conductance
TDP	Total dissolved phosphorus
USEPA	U.S. Environmental Protection Agency