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Puget Sound Groundwater Toxics Loading Analysis: Direct Discharge Pathway

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Quality Assurance Project Plan

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EAP: Environmental Assessment Program

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Abstract

The Washington State Department of Ecology (Ecology) is participating in a multi-phase effort to inventory and quantify toxic chemical loads to Puget Sound. One goal of this effort is to gain a better understanding of the relative significance of the various environmental pathways that deliver toxics to the Sound. The analysis described in this Quality Assurance Project Plan is intended to develop quantitative, upper-bound estimates of the amount of toxic chemicals delivered to the Puget Sound marine boundary by direct groundwater discharge. Estimates of annual toxic load will be developed using existing information; no field sampling will be conducted during this project.

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 completing the study, Ecology will post the final report of the study to the Internet.

Project Background

In response to a state initiative to restore and protect Puget Sound, the Puget Sound Partnership and the Washington State Department of Ecology (Ecology) are leading a multi-phase effort to inventory and quantify toxic chemical loads to the Sound (Figure 1). This effort will improve our understanding of the *relative* significance of the different pathways that deliver chemicals of concern to the marine environment (e.g., discharge from streams and rivers, direct air deposition, direct releases from municipal treatment plants). Refining quantitative loading estimates for the various contributing pathways will guide decisions about how best to direct resources for controlling toxic loading within the basin.

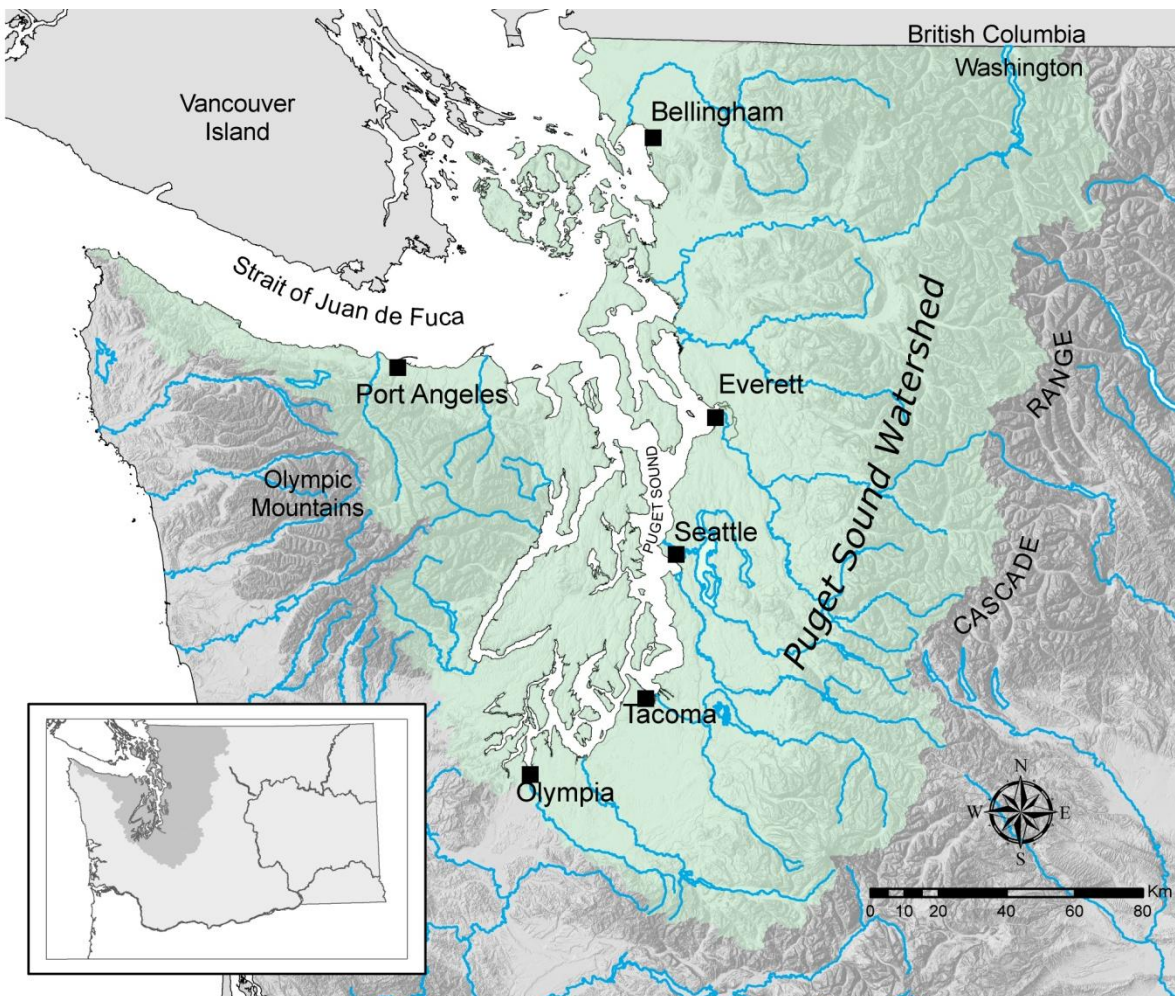


Figure 1. Puget Sound Watershed.

In 2007, a consortium of partners published initial estimates of toxic chemical loads to the Sound for many of the major transport pathways (Hart Crowser et al., 2007). This Phase 1 effort relied on readily accessible data to estimate chemical loading to Puget Sound. The authors of the report acknowledged in their conclusions that there remained a number of significant gaps in determining an accurate toxics budget for the Sound.

The 2007 Phase 1 report included a specific recommendation for the development of loading estimates for *direct* groundwater discharge to the marine shoreline of the Sound. Although the authors acknowledged the potential for the groundwater pathway to contribute a significant toxicant load at the local scale, this pathway was not addressed due to a lack of available resources and data. *Indirect* groundwater contributions of toxic chemicals to freshwater streams and rivers draining to the Sound were assumed to be reflected in the estimates presented for the surface runoff pathway (Hart Crowser et al., 2007).

In light of the mobility characteristics of many of the chemicals of concern, and the assumed contaminant attenuation capacity of subsurface sediments, the transport of toxic chemicals to the Sound via direct groundwater discharge is likely to represent a comparatively minor component of the overall basin loading budget. However, to date this assumption has not been confirmed by a formal technical analysis. Failure to adequately account for all potential pathways of toxics loading to the Sound could hamper future efforts to manage and restore this critical resource.

Project Description

The purpose of this project is to develop quantitative estimates of the annual toxic chemical load delivered to the Puget Sound marine boundary¹ by direct advective groundwater transport. This analysis will be performed for a specific list of toxic chemicals of concern (COCs) previously identified by the Phase 1 project team (Hart Crowser et al., 2007). If successful, this project will:

- Estimate the probable upper limit of annual toxic chemical loading to Puget Sound via direct discharge of groundwater.
- Improve our understanding of the relative contribution of the direct groundwater discharge pathway in comparison to other toxic loading pathway estimates.
- Provide data to support refinements to Ecology's Puget Sound Toxics Box Model (Pelletier and Mohamedali, 2009).

The limited time and budget available for this project dictate that this analysis will rely on existing information; no new field monitoring data or measurements will be collected during the course of this exercise. Because of (1) the complexity and geographic scope of the problem, (2) the limitations and biases inherent in the readily available data sets, and (3) the significant potential for the attenuation of dissolved-phase COC concentrations between the point of measurement and the marine shoreline, the primary focus of this analysis will be to develop reasonably defensible *upper-bound* estimates of the direct groundwater discharge contribution to the overall Puget Sound toxics budget. If the upper-bound loading values suggest the direct advective groundwater transport pathway may contribute a significant proportion of the overall toxic load to the Sound (or to a sub-basin of the Sound), additional investigation may be recommended.

The following technical objectives will be undertaken in support of the project goals described above:

- Assemble and evaluate information regarding direct groundwater volume discharge rates to the Sound from previously published research.
- Assemble, screen, and evaluate readily available near-shore groundwater toxics concentration data. For areas where data on groundwater toxics concentrations are limited, concentration assumptions may be extrapolated from adjacent areas, or drawn from scientific literature.
- Integrate volumetric flow rate and water quality concentration data to develop estimates of annual mass loading rates for the COCs listed in Table 1. If adequate data are available, loading estimates will be calculated for each of the 14 sub-basins designated for the loading analysis (Figure 2).
- Discuss sources of uncertainty and bias in the groundwater loading estimates.

¹ For this groundwater-focused evaluation, the marine boundary of Puget Sound is defined as a vertical surface extending downward from the marine shoreline. The analysis will predict the annual groundwater-borne mass flux delivered to this vertical boundary, but not beyond.

Table 1. Loading Analysis Chemicals of Concern (COCs).

Chemicals of Concern
<u>Metals</u> Arsenic Cadmium Copper Lead Mercury Zinc
<u>Petroleum Hydrocarbons</u> Diesel Range Organics (DRO) Gasoline Range Organics (GRO) Lube Oil Oil and Grease (both petroleum and non-petroleum)
<u>Low molecular weight polyaromatic hydrocarbons (LPAH)</u> Acenaphthene Acenaphthylene Anthracene Fluorene Naphthalene Phenanthrene
<u>High molecular weight polyaromatic hydrocarbons (HPAH)</u> Benz(a)anthracene (BaA) Benzo[a]pyrene (BaP) Benzo(b)fluoranthene (BbF) Benzo[g,h,i]perylene (BghiP) Benzo[k]fluoranthene (BkF) Chrysene Dibenzo[a,h]anthracene (DbahA) Fluoranthene Indeno[1,2,3-c,d]pyrene (IdP) Pyrene
<u>DDT and derivative/metabolites</u> 2,4-DDD 2,4-DDE 2,4-DDT 4,4-DDD 4,4-DDE 4,4-DDT
Polychlorinated Dioxins/Furans
Polychlorinated biphenyls (PCBs)
Polybrominated diphenyl ethers (PBDEs)
Triclopyr
Bis(2-ethylhexyl)phthalate (DEHP)
Nonylphenol

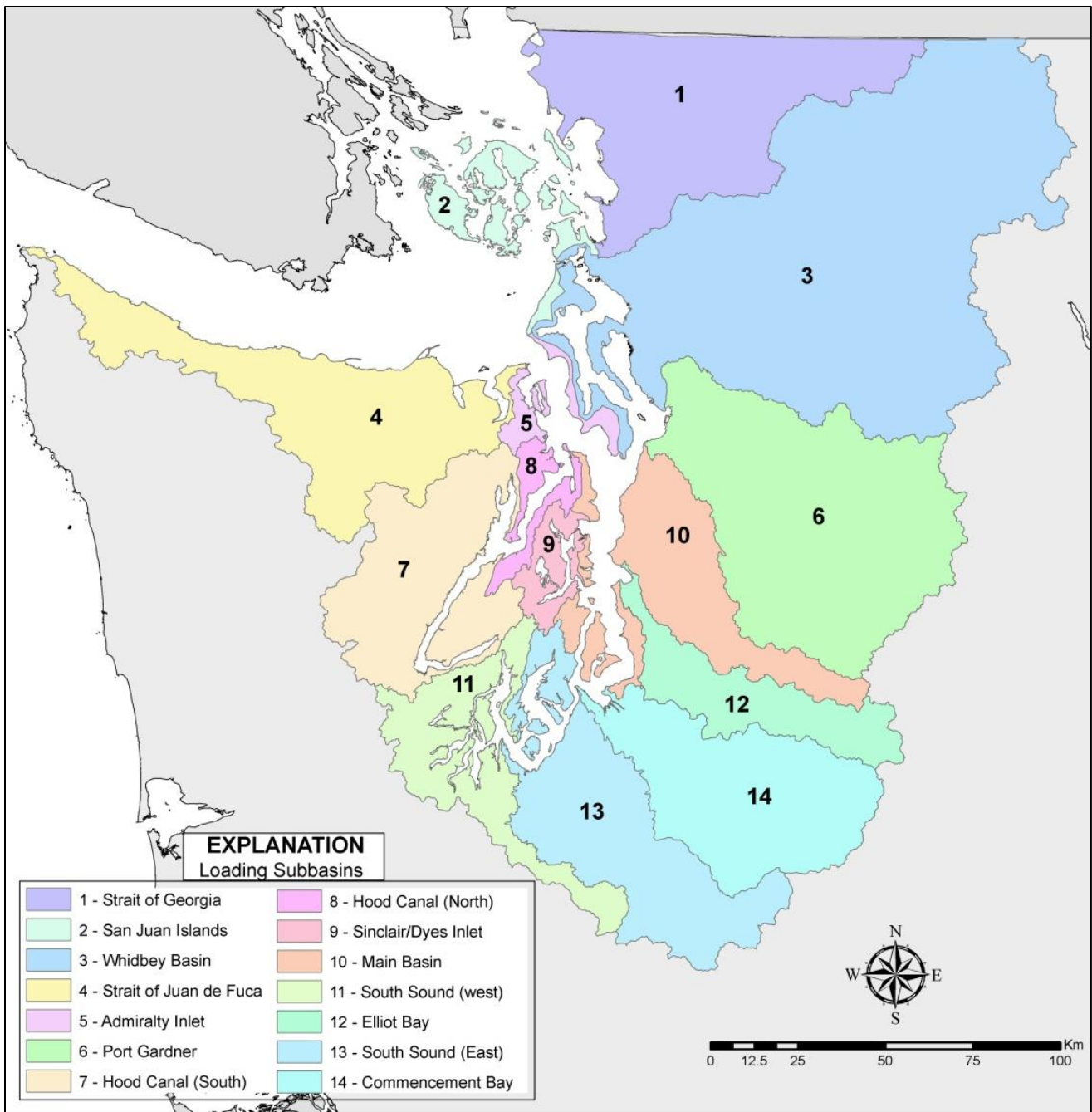


Figure 2. Puget Sound Sub-basin Map.

Organization and Schedule

The following people are involved in this project. All are employees of the Washington State Department of Ecology.

Table 2. Organization of Project Staff and Responsibilities.

Staff	Title	Responsibilities
Dave Serdar TSU-SCS-EAP Phone: 360-407-7384	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Charles F. Pitz GFFU-SCS-EAP Phone: 360-407-6775	Project Manager/ Principal Investigator	Writes the QAPP. Assembles, analyzes, and interprets data. Writes the draft report and final report.
Martha Maggi GFFU-SCS-EAP Phone: 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-EAP 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-EAP 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.
William R. Kammin EAP Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.
Mindy Roberts MISU-SCS-EAP Phone: 360-407-6804	Technical Advisor	Provides technical guidance to support analysis.
Greg Pelletier MISU-SCS-EAP Phone: 360-407-6485	Technical Advisor	Provides technical guidance to support analysis.
Dale Norton TSU-SCS-EAP Phone: 360-407-6765	Technical Advisor	Provides technical guidance to support analysis.

TSU: Toxics Studies Unit
 SCS: Statewide Coordination Section
 EAP: Environmental Assessment Program.
 GFFU: Groundwater, Forests and Fish Unit
 WOS: Western Operations Section
 MISU: Modeling and Information Support Unit
 QAPP: Quality Assurance Project Plan.

Table 3. Proposed Project Schedule.

Final report	
Author lead	Charles F. Pitz
Schedule	
Draft due to supervisor	December 1, 2010
Draft due to client/peer reviewer	December 15, 2010
Draft due to external reviewer(s)	December 31, 2010
Final (all reviews done) due to publications coordinator	January 31, 2011
Final report due on web	February 28, 2011

Analysis Methods

The annual toxic load delivered by direct groundwater discharge to the Puget Sound marine boundary will be calculated for each sub-basin for each COC by integrating estimates of the volumetric rate of subsurface discharge from that sub-basin with water quality concentration data, by solving a form of Equation 1:

$$F_M = \frac{Q_{DD} * C_{COC}}{1E+9} \quad \text{Eq. 1}$$

where:

F_M = the estimated total annual mass flux of the COC delivered to the sub-basin marine boundary (kg/year).

Q_{DD} = the estimated direct volumetric groundwater discharge rate to the sub-basin marine boundary (L/year).

C_{COC} = the estimated dissolved concentration of the COC in groundwater in the vicinity of the sub-basin shoreline (ug/L).

where:

kg = kilograms

ug = micrograms

L = liters

The proposed methods for deriving the Q_{DD} and C_{COC} terms in Equation 1 are discussed below.

Volumetric Groundwater Discharge

Estimates of the rate of direct volumetric groundwater discharge to the marine boundary of Puget Sound will be drawn from a U.S. Geological Survey (USGS) Regional Aquifer System Analysis (RASA) study performed in the 1990s (Vaccaro et al., 1998).

The USGS RASA study of the Puget Sound Lowland regional aquifer system presented a large-scale description of the hydrogeologic framework for the Quaternary-age alluvial, glacial, and interglacial sediments deposited across approximately 18,900 km² (7,300 mi²) of western Washington (Figure 3). The lateral and lower boundaries of the Puget Sound aquifer system are defined by pre-Quaternary age, low transmissivity bedrock units. With the exception of the northwestern shoreline of the Olympic Peninsula, and a small portion of southern British Columbia, the extent of the RASA study area is closely coincident with the surface runoff boundaries and marine shoreline of the Puget Sound basin (Figures 1 and 3).

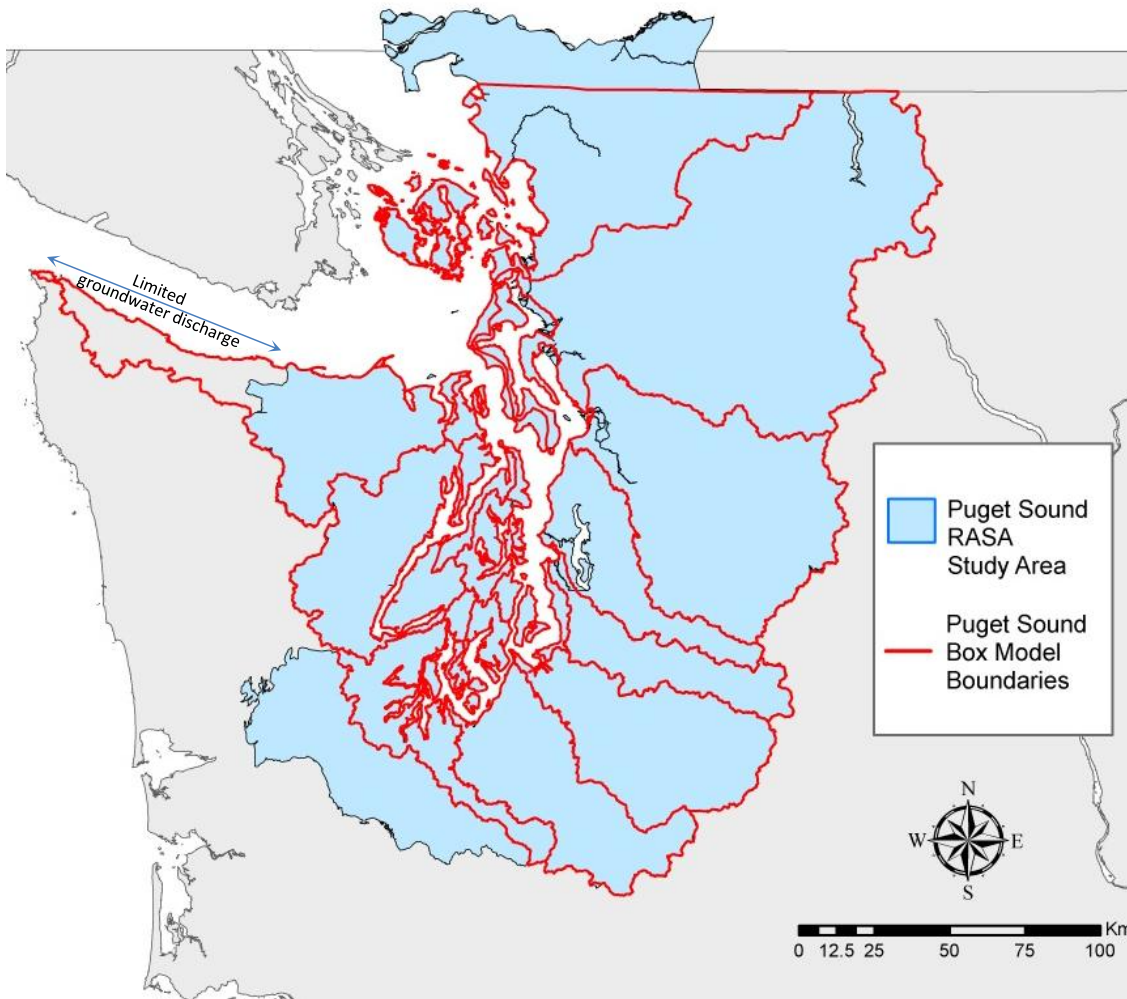


Figure 3. USGS RASA Study Area.

During their study, Vaccaro and coauthors characterized groundwater occurrence and flow, and developed a regional-scale water budget for the Puget Sound aquifer system. The water budget included estimates of groundwater discharge to seeps and springs, baseflow discharge to freshwater streams, and discharge to saltwater. Although a large percentage of groundwater flow was judged to discharge to rivers and streams prior to reaching the marine shoreline, Vaccaro and his coauthors estimated that between 2.832×10^3 to 2.832×10^4 L/sec (100 to 1000 ft³/sec) of groundwater directly discharges to saltwater from the aquifer system².

The regional scale of the Puget Sound RASA study precluded specific estimates of direct discharge at any given point along the marine shoreline. For this loading analysis, the following two-step method will be used to apportion the RASA direct discharge estimates:

- Using GIS tools, define a 1500-meter-wide (~0.9 mi) *recharge zone* inland of the Puget Sound shoreline for each sub-basin.

² There are an estimated 3621 km (2,250 mi) of marine shoreline within the RASA study area

- Using the USGS Puget Sound RASA annual groundwater recharge rate spatial data (USGS, 1998), solve for Equation 2:

$$Q_{DD} = Q_{DD\ RASA} * \frac{R_{SB\ RZ}}{R_{RASA\ RZ}} \quad \text{Eq.2}$$

where:

Q_{DD} = the estimated direct volumetric groundwater discharge rate to a sub-basin marine boundary (L/sec).

$Q_{DD\ RASA}$ = the estimated direct volumetric groundwater discharge rate to saltwater for the entire RASA study area (L/sec)(lower bound = 2.832×10^3 L/sec; upper bound = 2.832×10^4 L/sec).

$R_{SB\ RZ}$ = the estimated average annual volume of recharge entering the sub-basin near-shore *recharge zone* (L/year).

$R_{RASA\ RZ}$ = the estimated average annual volume of recharge entering the near-shore *recharge zone* for the entire RASA study area (L/year).

This method assumes that the proportional rate of recharge in the near vicinity of the Puget Sound shoreline is an indicator of the local hydrogeologic and climatic setting, and is therefore an approximate surrogate for the proportional rate of direct discharge likely to occur along each sub-basin shoreline. The method also assumes that the total annual rate of direct discharge has not changed significantly since the RASA estimates were developed in the 1990's (due to changes in land cover, climatic condition, or recharge rate).

No direct groundwater discharge will be estimated for the northwestern shoreline of the Olympic Peninsula that lies west of the RASA study area boundary (Figure 3). Low transmissivity bedrock units occur at or near the land surface throughout most of this area, therefore the amount of groundwater flow and discharge to the marine shoreline from this area is assumed to be negligible.

Chemical Data

Data Sources

Groundwater quality concentration data for the COCs listed in Table 1 will be drawn primarily from two publicly available, regional-scale data sources: (1) Ecology's Environmental Information Management (EIM) system, and (2) USGS's National Water Information System (NWIS). Locally-administered groundwater databases (e.g. King County Groundwater Database) will also be queried where readily available. The data sets queried from these systems will be processed and analyzed using standard database, spreadsheet, and GIS software programs (e.g., Microsoft Access 2007, Microsoft Excel 2007, ESRI ArcMap 9.2).

Data Screening

When compiling groundwater data for the loading analysis, the following data screening steps and assumptions will be employed:

- All groundwater concentrations will be normalized to a common concentration unit.
- Samples that are qualified specifically due to blank contamination will be omitted.
- The concentration value reported for all results qualified as estimates (e.g. “J” qualified) will be used without modification.
- To better reflect in situ aquifer conditions, monitoring samples that are qualified as collected after treatment or mixing will be omitted. In many cases, the point of collection for a sample is not designated; in these cases the sample will be assumed to reflect in situ subsurface conditions.
- To better reflect current conditions, sample results older than 1990 will be omitted from the loading analysis. In cases where there are multiple groundwater sample results at a unique monitoring station, the most recent sample result will be used for the loading analysis.
- To better reflect the mobile chemical fraction in the subsurface, unfiltered samples will be omitted from the loading analysis, unless insufficient data are available to develop representative statistics. In many cases, the level of filtration of a groundwater sample is not designated; in these cases the sample will be assumed to represent a dissolved-phase condition.
- To better reflect conditions that represent the quality of groundwater in the near vicinity of the marine shoreline, the available data sets will be screened using GIS tools to identify results only collected within a *buffer zone* extending 500 meters (1640 feet) inland of the shoreline (regardless of well depth). On the basis of the subsurface mobility characteristics of the Table 1 chemicals of concern, it is assumed that many of the contaminants are not likely to be transported over distances >500 meters before subsurface attenuation effects (e.g. sorption, biodegradation, dispersion) largely reduce the dissolved phase concentrations below detectable levels (Spitz and Moreno, 1996; Kresic, 2007; U.S. EPA, 1989).

Statistical Analysis

Key descriptive percentile statistics (10th percentile, 25th percentile, median) will be generated for each COC in Table 1, for each sub-basin. No data transformation will be conducted prior to calculation of the percentile statistics. Percentile statistics will not be calculated in cases where there are <5 data values available for a parameter, for a sub-basin. Rules for extrapolating COC concentrations to areas with insufficient data are presented later in this QAPP.

Non-Detect Substitution Rules

A preliminary inventory of the water quality data available in the chosen databases indicates a significant percentage (50-100%) of the COC results are non-detects. The high proportion of non-detects is probably the result of several factors:

- Many of the COCs do not occur naturally in the groundwater environment,
- Many of the COCs exhibit a strong tendency to remain associated with the solid phase (due to low solubility, high sorption coefficients, high reactivity), limiting dissolved (aqueous) phase concentrations and transport away from source areas,

- Detection limits for older samples may have been higher than the COC concentrations routinely occurring in the environment.

Since the data sets being used for this loading analysis include monitoring results from a wide variety of projects, data originators, and time periods, individual reporting limit (RL) concentrations within any given subset of data can range over 3 to 4 orders of magnitude.

Because they do not represent a quantified concentration, non-detect results cannot be directly used for developing concentration statistics. A number of possible statistical substitution methods for non-detects have been suggested for this problem (e.g., U.S. EPA, 2009). Each of these substitution methods can introduce bias into the results, especially when the proportion of non-detects is significantly greater than 50%. The loading estimates developed using Equation 1 can be highly sensitive to the substitution assumptions for non-detects, potentially predicting mass flux values far above what actually occurs in the environment.

To address this problem for the loading analysis, three different non-detect substitution rules will be tested to evaluate the influence of substitution on the loading analysis results [similar to techniques described by Pelletier and Mohamedali, (2009)]. The three methods include:

- Method 1 - A concentration of 0.5RL will be substituted for all non-detect results in a data set, regardless of the RL concentration.
- Method 2 - A concentration equal to the lowest RL within a given data set will be substituted for all non-detect results in that data set.
- Method 3 - All non-detect results will be omitted from further analysis.

Cumulative frequency distribution analyses will be used to evaluate the effect of the substitution methods on the data distribution, to guide selection of the rules used for final calculation of load. All loading estimates calculated using >50% non-detect substitutions will be flagged.

Data Set Bias

Washington State does not operate an ambient or randomized groundwater quality monitoring program that would support the development of broad regional estimates of COC groundwater concentrations entering Puget Sound. In the absence of a reliable regional-scale ambient data set, it is important to recognize inherent biases in the chemical data that are available. Without adjustment these biases could significantly distort the results of the loading analysis.

Queries of the selected data systems indicate that a significant majority of the data that will qualify for the loading analysis will be drawn from the Ecology EIM system. Because of the regulatory focus of Ecology as an agency [for example, implementing monitoring studies in support of the Model Toxics Control Act (MTCA) or state Dangerous Waste regulations], the groundwater toxic results in the EIM database are assumed to be strongly biased towards (and spatially clustered around) industrial or commercial land uses, sites, or facilities that are known or suspected to have point-source-related toxic contamination. Without modification, concentration statistics developed from data sets built primarily with EIM data would likely bias

the loading calculations high, since these values would mostly represent a comparatively small, „impacted’ portion of the land adjacent to the marine shoreline.³

A small set of COC data results are available within the *buffer zone* from the USGS NWIS database. Although the USGS serves as a technical consultant for the U.S. EPA on studies of contaminated federal facilities (e.g., military installations under investigation through the Superfund or Comprehensive Environmental Response, Compensation, and Liability Act program), most of the *buffer zone* COC data values present in the NWIS database represent ambient groundwater conditions away from known contaminant sources (e.g., Kahle and Olsen, 1995; Thomas et al., 1997; Greene, 1997; Drost et al., 1998).

County-administered groundwater monitoring databases generally contain data that represent larger-scale ambient or nonpoint conditions; in most cases known locations of point source contamination are deliberately avoided during sampling for ambient monitoring programs. With the exception of inorganics, however, locally-operated monitoring programs infrequently test for the COCs. This is typically due to the high cost of analysis for many of these parameters versus the low likelihood of detection (due to the generally hydrophobic character of the organic contaminants). These factors, and the relatively limited number of locally-administered groundwater quality monitoring programs in the Puget Sound area, limit the size of the data sets available from these sources.

Chemical Concentration Assumptions

Table 4 summarizes the data bias assumptions for the different chemical data sources that will be used during the loading analysis.

Table 4. Chemical Data Bias Assumptions.

EIM Data		NWIS Data		Local (County) Data	
Inorganic COCs	Organic COCs	Inorganic COCs	Organic COCs	Inorganic COCs	Organic COCs
Assume all data values represent <i>impacted</i> conditions		Assume all data values represent <i>ambient</i> conditions		Assume all data values represent <i>ambient</i> conditions	

Equation 1 requires that a COC concentration be assigned to represent the bulk dissolved-phase condition for each toxic parameter for the groundwater discharging from the sub-basin. Assigning a single concentration value to a sub-basin’s discharge, however, may not adequately represent variations in conditions between contaminated and ambient areas, or beneath different land uses.

³ The large number of the data values involved, the limited project schedule, and the limited metadata associated with the monitoring results preclude an effort to specifically identify, select out, and statistically evaluate only “up-gradient” or “background” wells at contaminated facilities. It should also be noted that even within the EIM data sets, non-detects represent a large proportion of the available results.

To adjust for the bias introduced by the large percentage of potentially impacted data results, and to better reflect ambient conditions away from point sources of toxic contamination, GIS mapping tools will be used to categorize each sub-basin shoreline into three major classes: (1) *impacted*, (2) *urban-ambient*, and (3) *non-urban ambient*.

Using the criteria outlined in Table 4, the approximate proportion of the marine shoreline in each sub-basin that is hydraulically downgradient of *impacted buffer zone* areas will be determined (assuming groundwater flow is perpendicular to the shoreline in near-shore areas). (See Figure 4).

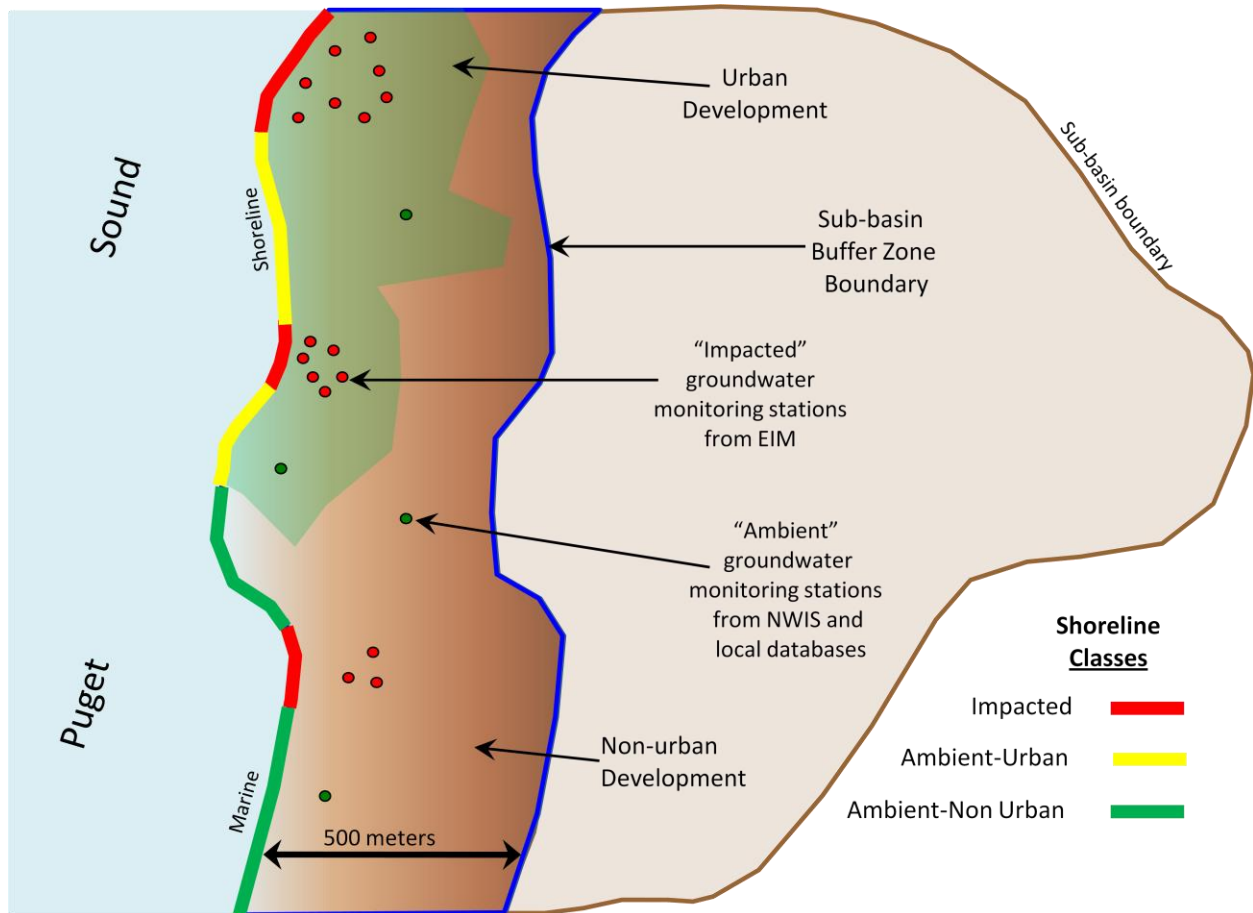
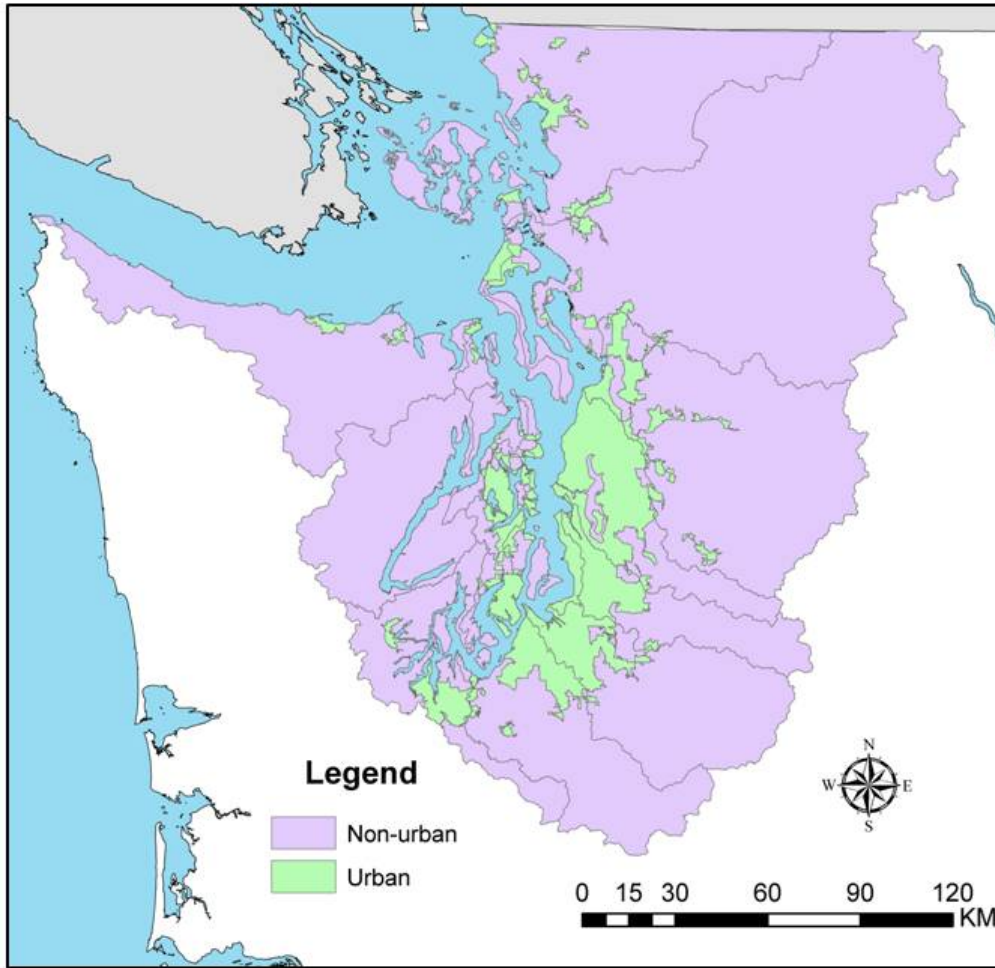


Figure 4. Method for Assigning C_{COC} Concentrations for Loading Calculations.

To reflect the assumption that ambient COC conditions are likely to be different beneath urbanized versus non-urbanized areas, the sub-basin shoreline will be further subdivided into *ambient-urban* and *ambient non-urban* sections, using the consolidated U.S. Census Bureau land cover spatial data shown on Figure 5. A statistically representative C_{COC} concentration for each of the three sub-basin shoreline classes will then be integrated into Equation 1 as described below.



Data Source: Ecology, 2010, GIS Spatial Data, from U.S. Department of Commerce, U.S. Census Bureau, Geography Division

Figure 5. Urban/Non-Urban Land Cover – Puget Sound Basin.

Sub-basin Mass Flux Estimation Methods

The annual COC mass flux delivered to the three different classes of a sub-basin shoreline will be integrated by modifying Equation 1 to Equation 3 (see also Figure 4 and Table 5):

$$F_M = \frac{\left[\left(Q_{DD} * \frac{SL_{IMP}}{SL_{TOT}} \right) * C_{IMP} \right] + \left[\left(Q_{DD} * \frac{SL_{UA}}{SL_{TOT}} \right) * C_{UA} \right] + \left[\left(Q_{DD} * \frac{SL_{NUA}}{SL_{TOT}} \right) * C_{NUA} \right]}{1E+9} \quad \text{Eq. 3}$$

where:

F_M = the estimated total annual mass flux of the COC delivered to the sub-basin marine boundary (kg/year).

Q_{DD} = the estimated direct volumetric groundwater discharge rate to the sub-basin marine boundary (L/sec).

SL_{IMP} = the total length of sub-basin shoreline classified as impacted (meters).

SL_{UA} = the total length of sub-basin shoreline classified as urban-ambient (meters).

SL_{NUA} = the total length of sub-basin shoreline classified as non-urban-ambient (meters),
 SL_{TOT} = the total length of sub-basin shoreline (meters).
 C_{IMP} = the estimated COC concentration for sub-basin *impacted* areas (ug/L) (see Table 5).
 C_{UA} = the estimated COC concentration for sub-basin *urban-ambient* areas (ug/L) (see Table 5).
 C_{NUA} = the estimated COC concentration for sub-basin *non-urban-ambient* areas (ug/L) (see Table 5).

Table 5. COC Concentration Assumption Rules.

C_{IMP}		C_{UA}		C_{NUA}	
If sub-basin <i>impacted</i> sample set $n \geq 5$	If sub-basin <i>impacted</i> sample set $n < 5$	If sub-basin <i>urban ambient</i> sample set $n \geq 5$	If sub-basin <i>urban ambient</i> sample set $n < 5$	If sub-basin <i>non-urban ambient</i> sample set $n \geq 5$	If sub-basin <i>non-urban ambient</i> sample set $n < 5$
Median (50 th percentile) of pooled sub-basin buffer zone <i>impacted</i> sample concentrations	$C_{IMP} = 0$	Median (50 th percentile) of pooled sub-basin buffer zone <i>urban ambient</i> sample concentrations	Median (50 th percentile) of pooled Puget Sound-wide buffer zone <i>urban ambient</i> sample concentrations, if sample set $n \geq 15$	Median (50 th percentile) of pooled sub-basin buffer zone <i>non-urban ambient</i> sample concentrations	Median (50 th percentile) of pooled Puget Sound-wide buffer zone <i>non-urban ambient</i> sample concentrations, if sample set $n \geq 15$
			Otherwise		
			25 th percentile of pooled Puget Sound-wide buffer zone <i>impacted</i> sample concentrations, if sample set $n \geq 10^*$		
				10 th percentile of pooled Puget Sound-wide buffer zone <i>impacted</i> sample concentrations, if sample set $n \geq 10^*$	

*If the pooled Puget Sound-wide buffer zone *impacted* sample set $n < 10$, no load will be calculated.

The Q_{DD} value in Equation 3 will be varied between the lower (2.832×10^3 L/sec) and upper (2.832×10^4 L/sec) bound RASA marine discharge estimates to bracket the loading range.

Study Design Limitations

The loading analysis described in this QAPP relies on a number of simplifying assumptions which can introduce uncertainty or bias into the final mass flux estimates. Some of the limitations of the study design described in this plan are listed here:

- The analysis does not address or estimate any dissolved COC concentration attenuation that may occur between the point of measurement and the marine boundary.
- The analysis does not address or estimate the dissolved phase groundwater toxic load that actually discharges to the marine water column of Puget Sound. Significant reductions in contaminant concentrations and mass flux due to tidal mixing and biogeochemical processing may occur along the groundwater flow path between the marine boundary and the actual point of discharge (which may be many meters offshore of the shoreline).
- The assumptions regarding the areal distribution and volume of discharge may be invalid.
- Impacted sample locations may have been remediated since measurement.
- The generalizing assumptions about data bias might be invalid. EIM samples considered representative of impacted conditions may actually represent background conditions in the near vicinity of a contaminated site (most likely urban-ambient), and other samples assumed to represent ambient conditions may in fact have been collected in the vicinity of a contaminant source.
- The metadata that would allow more precise screening of the data sets are rarely recorded. For example, samples that are assumed to represent dissolved phase conditions may actually be biased by the presence of entrained particulates that contain sorbed COCs that would otherwise be immobile in the subsurface.
- The assumption that all samples represent in-situ conditions may be invalid (for example concentrations of redox sensitive species may have been biased by sample handling procedures).

Project Deliverables

A technical report will be prepared on completion of the loading analysis. The report will document:

- Description and objectives of the project.
- The types and sources of data used for the analysis.
- The analysis methods and assumptions.
- Estimates of the annual COC mass loading range for each of the 14 sub-basins.
- Data limitations and sources of uncertainty in the loading estimates.

Following internal review by the EAP project team, a draft of the final report will be presented for external review and comment. A final report will be published after all external review comments have been addressed.

References

- Drost, B.W., Turney, G.L., Dion, N.P., and Jones, M.A., 1998. Hydrology and quality of ground water in northern Thurston County, U.S. Geological Survey Water-Resources Investigations Report 92-4109 (revised), 230 p. http://pubs.er.usgs.gov/publication/wri924109_1994
- Greene, K.E., 1997. Ambient Quality of Ground Water in the Vicinity of Naval Submarine Base Bangor, Kitsap County, Washington, 1995, U.S. Geological Survey Water-Resources Investigations Report 96-4309, 50 p. <http://pubs.er.usgs.gov/publication/wri964309>
- Hart Crowser, Washington State Department of Ecology, U.S. Environmental Protection Agency, and Puget Sound Partnership, 2007. Control of Toxic Chemicals in Puget Sound – Phase 1: Initial Estimate of Loadings, Washington State Department of Ecology Publication No. 07-10-079, 188 p. www.ecy.wa.gov/biblio/0710079.html
- Kahle, S.C. and Olsen, T.D., 1995. Hydrogeology and Quality of Groundwater on Guemes Island, Skagit County, Washington, U.S. Geological Survey, Water Resources Investigations Report 94-4236, 89 p. <http://pubs.er.usgs.gov/publication/wri944236>
- Kresic, N., 2007. Hydrogeology and Groundwater Modeling, Second Edition, CRC Press, Boca Raton, FL, 807 p.
- Pelletier, G. and Mohamedali, T., 2009. Control of toxic chemicals in Puget Sound – Phase 2: Development of simple numerical models, The long-term fate and bioaccumulation of polychlorinated biphenyls in Puget Sound, Washington State Department of Ecology Publication No. 09-03-015, 205 p. www.ecy.wa.gov/biblio/0903015.html
- Spitz, K. and Moreno, J., 1996. A Practical Guide to Groundwater and Solute Transport Modeling, John Wiley & Sons, Inc., New York, New York, 461 p.
- Thomas, B.E., Wilkinson, J.M., and Embrey, S.S., 1997. The ground-water system and ground-water quality in western Snohomish County, Washington, U.S. Geological Survey Water-Resources Investigations Report 96-4312, 218 p. <http://pubs.er.usgs.gov/publication/wri964312>
- U.S. EPA, 1989. Transport and Fate of Contaminants in the Subsurface. U.S. Environmental Protection Agency. Seminar Publication, EPA/625/4-89/019, 148 p.
- U.S. EPA, 2009. Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities – Unified Guidance. U.S. Environmental Protection Agency, 888 p. www.epa.gov/osw/hazard/correctiveaction/resources/guidance/sitechar/gwstats/unified-guid.pdf
- USGS, 1998. U.S. Geological Survey, Water Resources Division, Puget Sound Aquifer Recharge Rate Spatial Data.
- Vaccaro, J.J., Hansen, A.J. Jr., and Jones, M.A., 1998. Hydrogeologic Framework of the Puget Sound Aquifer System, Washington and British Columbia, U.S. Geological Survey Professional Paper 1424-D, 77p + plate. http://pubs.er.usgs.gov/djvu/PP/pp_1424_d.djvu

Appendix. Glossary, Acronyms, and Abbreviations

Glossary

Ambient: Background or away from point sources of contamination.

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.

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.

Reporting limit (RL): the lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision.

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.

10th percentile: A statistical number obtained from a distribution of a data set, above which 90% of the data exists and below which 10% of the data exists.

25th percentile: A statistical number obtained from a distribution of a data set, above which 75% of the data exists, and below which 25% of the data exists.

Median (50th percentile): A statistical number representing the middle value of a given set of ranked values.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

COCs	chemicals of concern
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
et al.	And others
GIS	Geographic Information System
i.e.	In other words
RL	Reporting limit
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Units of Measurement

ft	feet
kg	kilograms, a unit of mass equal to 1,000 grams.
kg/year	kilograms per year
km	kilometer, a unit of length equal to 1,000 meters.
l/s	liters per second (0.03531 cubic foot per second)
m	meter
ug/L	micrograms per liter (parts per billion)