Control of Toxic Chemicals in Puget Sound

Evaluation of Loading of Toxic Chemicals to Puget Sound by Direct Groundwater Discharge

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Control of Toxic Chemicals in Puget Sound

Evaluation of Loading of Toxic Chemicals to Puget Sound by Direct Groundwater Discharge

by

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Glossary, Acronyms and Abbreviations

Glossary

Advective flow (advection): The transport of a fluid or solute by the bulk motion of flowing groundwater.

Ambient: Background or away from point (discrete) sources of contamination.

Attenuation: The reduction in the concentration, mass, toxicity, mobility, or volume of a chemical due to chemical, biological, or physical processes.

Baseflow: Groundwater discharge to a surface stream or river. The component of total streamflow that originates from direct groundwater discharges to a stream.

Basin: Watershed. A drainage area 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.

Budget: A method for balancing exchanges (inputs and outputs) within a defined system.

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

K_d: Partition (or distribution) coefficient. The ratio of the amount of chemical mass that partitions between solid and liquid phases, at equilibrium. Higher K_d values correlate to lower chemical mobility in soils; lower values correlate to higher mobility.

K_{oc}: Soil organic carbon-water partition coefficient. K_{oc} is K_d normalized to the fraction of organic carbon in a soil. The ratio of the amount of chemical adsorbed in a soil per unit weight of organic carbon versus the chemical concentration in a solution adjacent to the soil, at equilibrium. K_{oc} is a useful index to predict the mobility of organic chemicals in soils. Higher K_{oc} values correlate to lower chemical mobility in soils; lower values correlate to higher mobility.

K_{ow}: Octanol-water partition coefficient. The ratio of the concentration of a chemical in octanol and in water at equilibrium, at a specified temperature. Octanol is an organic solvent that is used as a surrogate for natural organic matter. Higher K_{ow} values correlate to lower chemical mobility in soils; lower values correlate to higher mobility.

Loading: The input of a chemical mass into a waterbody.

Marine boundary: For this groundwater-focused evaluation, the marine boundary of Puget Sound is defined as a vertical surface extending downward from the marine shoreline.

Mass flux: A measure of the amount of mass transported (loaded) across a surface or into a defined receiving area in a given time period.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Point source: Source that discharges at a specific location.

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.

Sediment: Solid fragmented material (soil and organic matter) that is transported and deposited by water.

Submarine groundwater discharge (SGD): The discharge of fresh groundwater (and re-circulated marine water) from an aquifer to a marine waterbody, through the coastal sea floor.

Surface runoff: The flow of water over the surface of the ground occurring when rainfall is not absorbed into the soil or evaporated.

10th percentile: A statistic defining the value in a dataset that is greater than or equal to 10% of the values, and is less than or equal to 90% of the values.

25th percentile: A statistic defining the value in a dataset that is greater than or equal to 25% of the values, and is less than or equal to 75% of the values.

Median (50th percentile): A statistic that defines the middle value of a given set of ranked values.

Acronyms and Abbreviations

a.k.a.	Also known as
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act (also known as: Superfund)
CFD	Cumulative frequency distribution
CLARC	Cleanup Levels and Risk Calculations
COCs	Chemicals of concern
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DEHP	Bis(2-Ethylhexyl) phthalate
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
et al.	And others
GIS	Geographic Information System
HPAH	High molecular weight PAH
i.e.	In other words
LPAH	Low molecular weight PAH
NAWQA	National Water Quality Assessment
NWIS	National Water Information System
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ethers

PCB	Polychlorinated biphenyl
RL	Reporting limit
TCDD	2,3,7,8-tetrachlorodibenzodioxin
TCDF	2,3,7,8-tetrachlorodibenzofuran
USGS	U.S. Geological Survey

Units of Measurement

ft^3/sec	cubic feet per second
kg	kilograms, a unit of mass equal to 1,000 grams
kg/yr	kilograms per year
km	kilometer, a unit of length equal to 1,000 meters
km^2	square kilometer
L/kg	liters per kilogram
L/sec	liters per second (0.03531 cubic foot per second)
m	meter
mi	mile
mi^2	square mile
m^3/yr	cubic meter per year
mg/L	milligram per liter (parts per million)
ug/L	micrograms per liter (parts per billion)
%	percent

Abstract

In 2010-2011, the Washington State Department of Ecology developed quantitative estimates of the annual toxic chemical load delivered to Puget Sound by direct groundwater discharge. The analysis was performed for a priority list of 34 toxic chemicals of concern identified during Phase 1 of the *Control of Toxic Chemicals in Puget Sound* project. The results of this evaluation will help to:

- Estimate the maximum annual toxic chemical load likely to be delivered to Puget Sound via direct discharge of groundwater.
- Improve 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.

The report (1) describes the methods and assumptions used to develop the loading estimates and (2) discusses sources of uncertainty in the predictions. The loading values presented in the report best represent an upper-bound (worst-case) condition. Actual toxic loading to Puget Sound by direct groundwater discharge is likely significantly lower than the estimates presented.

In Phase 3 of the *Control of Toxic Chemicals in Puget Sound* project, the groundwater loading estimates presented in this report will be synthesized with loading estimates for other toxic delivery pathways. This information will support ongoing efforts to improve the accuracy of the overall Puget Sound Basin toxics budget.

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Introduction

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 various pathways that deliver chemicals of concern to the marine (saltwater) environment. Refining chemical loading estimates for each of these pathways will guide decisions about how best to direct resources for controlling toxics within the Puget Sound basin.

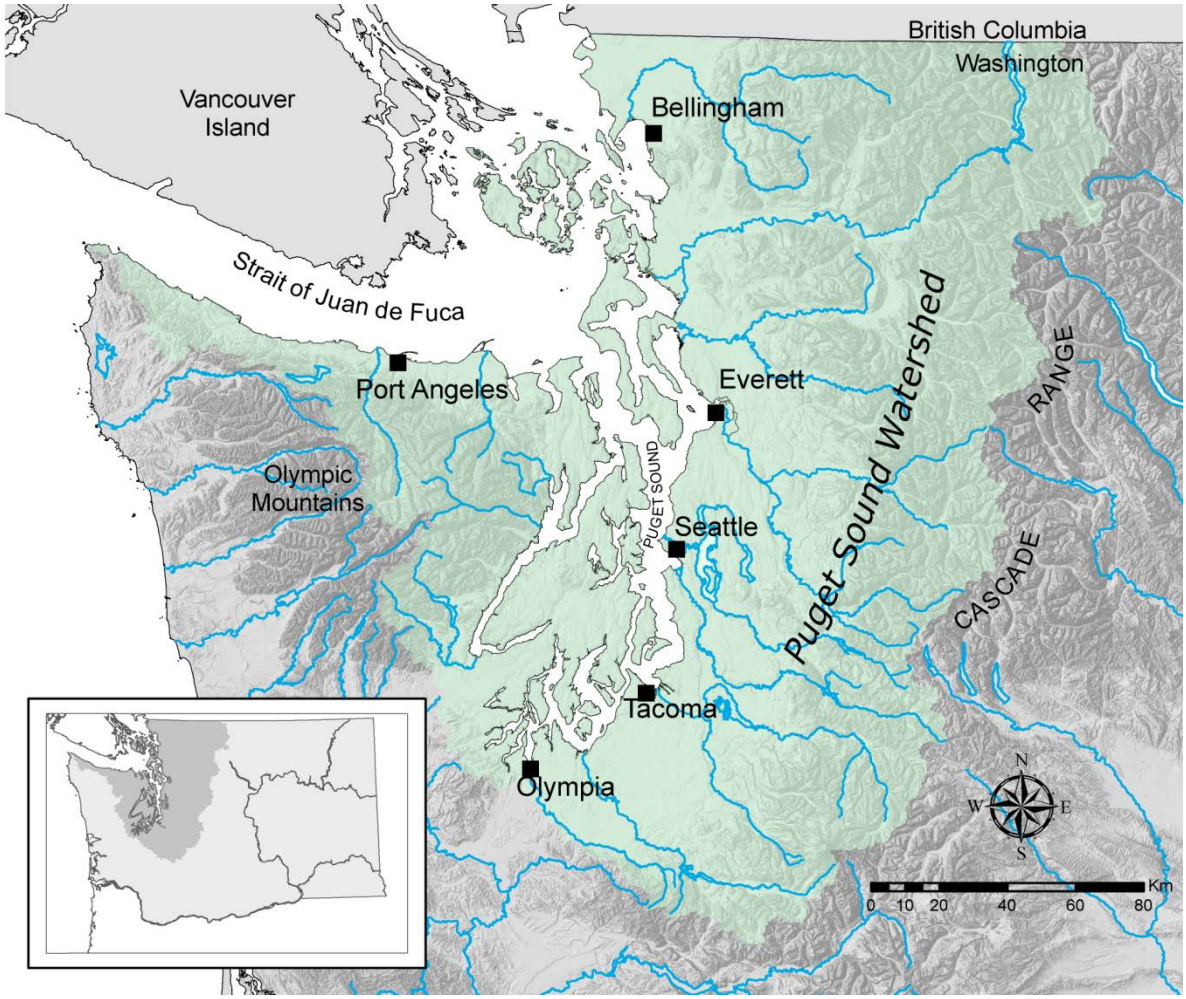

Figure 1. Puget Sound Watershed.

In 2007, a consortium of investigators 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 the marine basin. The authors of the report acknowledged in their conclusions that there remained a number of significant gaps in determining an accurate toxic chemical budget[1] for the Sound.

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

Additional studies were conducted between 2007 and 2009 to improve the Phase 1 loading estimates (Phase 2). The Phase 2 effort, however, did not include further attention to the groundwater pathway. 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. This assumption, however, has not been confirmed by a formal technical analysis. Failure to adequately account for all potential pathways of toxics loading could hamper future efforts to manage and restore Puget Sound.

Ecology will incorporate the results presented in this report into an up-to-date toxics loading synthesis for the Sound (Phase 3; see www.ecy.wa.gov/programs/wq/pstoxics/index.html, *Control of Toxic Chemicals in Puget Sound*).

[1] A chemical budget is a method of accounting for all the mass inputs and outputs of a chemical(s) of concern for a given water body of interest.

Project Description

The purpose of this project was to develop quantitative predictions of the annual toxic chemical load delivered *to the Puget Sound marine boundary*[2] by direct advective groundwater transport. The analysis was performed for a priority list of toxic chemicals of concern (COCs) previously identified by the Phase 1 project team (Table 1)(Hart Crowser et al., 2007).

The current project will help to:

- Estimate the maximum annual toxic chemical load likely to be delivered to Puget Sound via direct (submarine) discharge of groundwater.
- Improve 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 primary focus of this analysis was to develop reasonably defensible *upper-bound* estimates of annual toxic load. If the upper-bound loading values suggest the direct groundwater discharge pathway may contribute a significant proportion of the overall toxic load to the Sound (or to a subbasin of the Sound), additional investigation may be recommended in the Phase 3 synthesis report.

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

- Assemble and evaluate information about fresh groundwater 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 describing groundwater toxics concentrations are limited, extrapolate concentration assumptions from adjacent areas or secondary datasets.
- Integrate volumetric flow rate and water quality concentration data to develop estimates of annual mass-loading (mass flux) rates for the COCs listed in Table 1. If adequate data are available, calculate mass flux estimates for each of the 14 subbasins designated for the loading analysis (Figure 2).
- Discuss sources of uncertainty and bias in the groundwater loading estimates.

[2] 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 predicts an annual groundwater-borne mass flux delivered to this vertical boundary, but not beyond.

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

Chemicals of Concern
Metals Arsenic Cadmium Copper Lead Mercury Zinc
Petroleum hydrocarbons Diesel range organics (DRO) Gasoline range organics (GRO) Lube oil Oil and grease (both petroleum and non-petroleum)
Low molecular weight polyaromatic hydrocarbons (LPAH) Acenaphthene Acenaphthylene Anthracene Fluorene Naphthalene Phenanthrene
High molecular weight polyaromatic hydrocarbons (HPAH) 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
DDT and derivative/metabolites 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

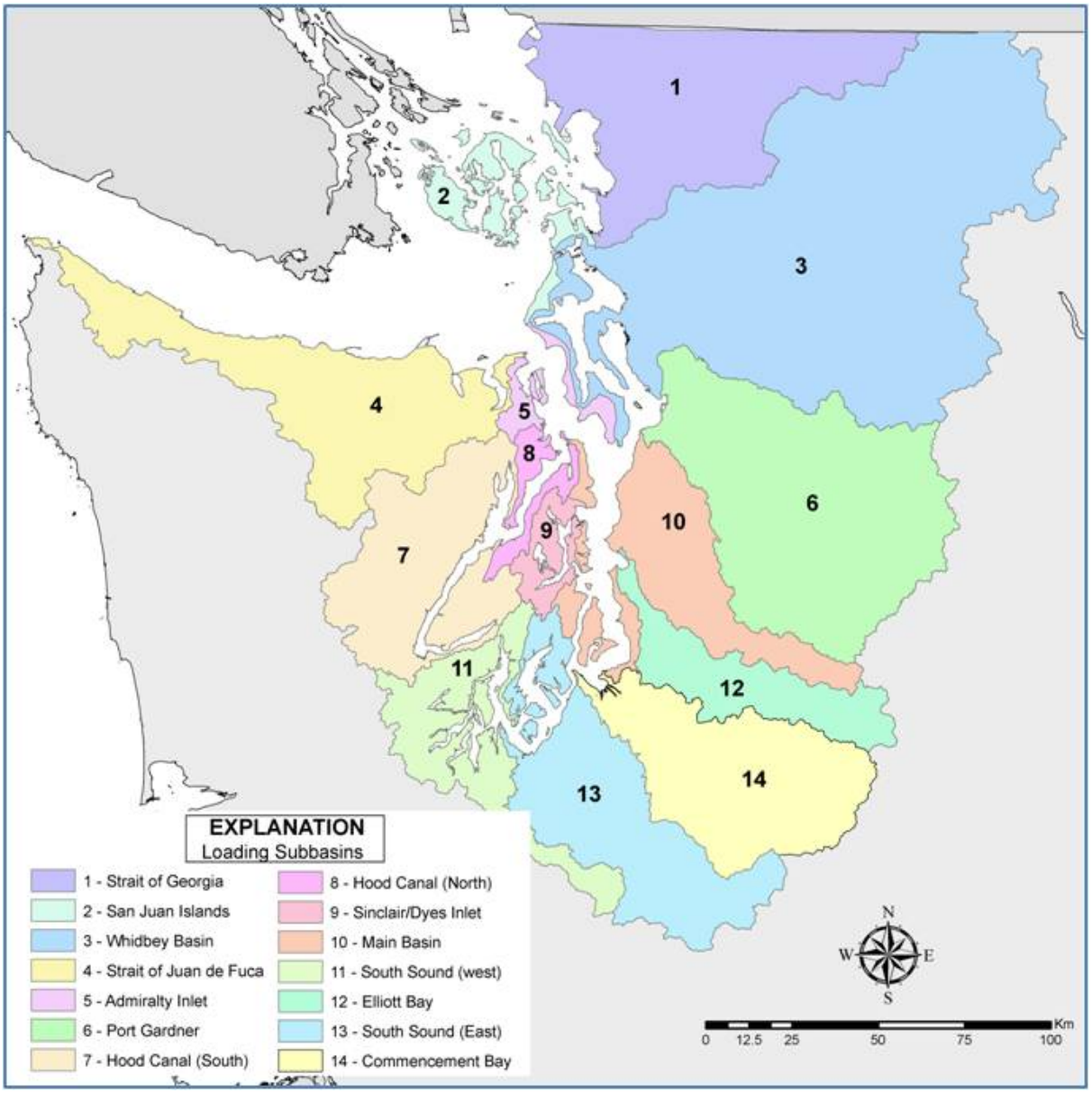

Figure 2. Map of Puget Sound Loading Subbasins.

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Analysis Methods

The annual toxic load delivered by direct groundwater discharge to the Puget Sound marine boundary was calculated for each COC with adequate data. The calculation integrated estimates of the volumetric rate of fresh groundwater discharge with water quality concentration data, by solving a form of Equation 1:

$$F_{PS} = \frac{Q_{DD} * C_{COC}}{1E+9} \qquad \text{Eq. 1}$$

where:

F_{PS} = the estimated total annual mass flux of the COC delivered to the Puget Sound marine boundary by direct groundwater discharge (kg/yr).
Q_{DD}= the estimated direct fresh groundwater discharge rate to Puget Sound (L/year).
C_{COC} = the estimated dissolved concentration of the COC in groundwater in the near vicinity of the marine boundary (ug/L).

where:

kg = kilograms
ug = micrograms
L = liters

The data sources and methods for deriving the Q_{DD} and C_{COC} terms in Equation 1 are described below.

Volumetric Groundwater Discharge

Estimates of the volumetric rate of direct groundwater discharge to the marine boundary of Puget Sound (Q_{DD}) were 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 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 km^2 (7,300 mi^2) 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).

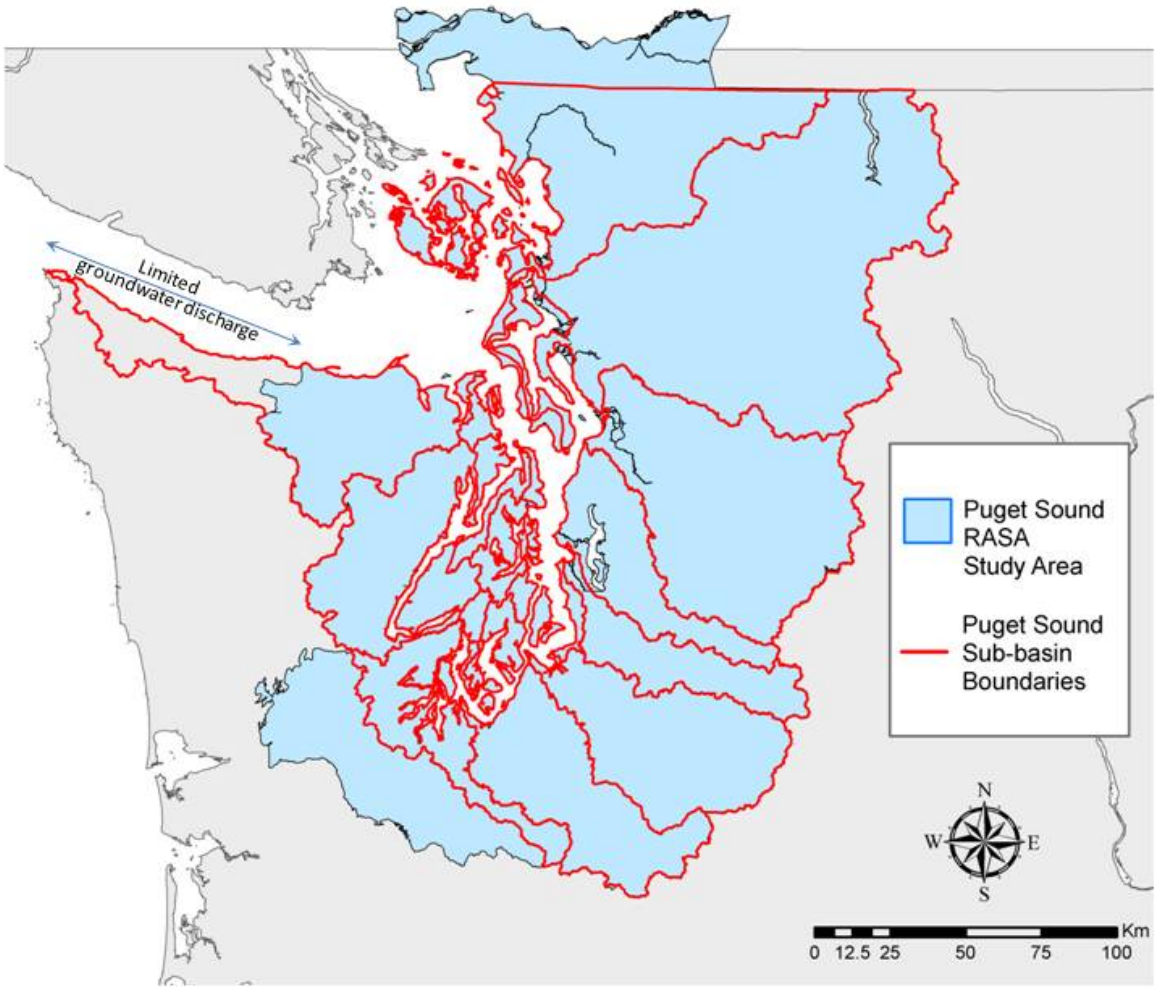

Figure 3. Study Area for the USGS Puget Sound Lowland Regional Aquifer System Analysis (RASA).

During their study, Vaccaro and co-authors characterized groundwater occurrence and flow, mapped the spatial distribution of estimated recharge, and developed a regional-scale water budget for the aquifer system as a whole. The water budget included estimates of groundwater discharge to seeps and springs, baseflow discharge to freshwater streams, and fresh groundwater discharge to saltwater. Although a large percentage of groundwater flow was judged to discharge to rivers and streams prior to reaching the marine shoreline, the authors of the RASA study estimated that between 2.832E+03 to 2.832E+04 L/sec (100 to 1000 ft^3/sec) of fresh groundwater discharges directly to saltwater from the aquifer system[3].

[3] There are an estimated 3,621 km (2,250 mi) of marine shoreline within the RASA study area. Approximately 97 km (~60 mi) of this total lies within Canada. Since this represents <3% of the study area shoreline total, and a significant portion of the near-shore Canadian area is comprised of bedrock, the 100-1000 ft^3/sec RASA estimate of *total* annual groundwater discharge to Puget Sound was not modified (i.e. proportionally reduced) for the current loading analysis.

The regional scale of the Puget Sound RASA study precluded specific estimates of direct groundwater discharge at any given point along the marine shoreline. For this loading analysis, the following three-step method was used to allocate the RASA fresh groundwater discharge total across the marine boundaries of the 14 subbasins of interest:

1. Use GIS tools to define a maximum 1500-meter-wide (~0.9 mi) *Recharge Zone* immediately inland of the Puget Sound shoreline. Define the *Recharge Zone* for each subbasin.[4]
2. Apply GIS tools to the Puget Sound RASA groundwater recharge spatial data (USGS, 1998; see Figure 13 in Vaccaro et al., 1998), to tabulate the average annual volume of recharge entering the groundwater system in the 1500-meter wide *Recharge Zone* (see Figure 4 for example).
3. Calculate the direct groundwater discharge rate from each subbasin shoreline using:

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

where:

$Q_{SB\ DD}$ = the estimated direct groundwater discharge rate to a subbasin marine boundary (L/sec).

$Q_{RASA\ DD}$ = the estimated fresh groundwater discharge rate for the entire RASA study area (low-flow scenario = 2.832E+03 L/sec; high-flow scenario = 2.832E+04 L/sec).

$R_{SB\ RZ}$ = the estimated average annual volume of recharge entering the near-shore subbasin *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).

Equation 2 uses information about the spatial distribution of recharge near the marine shoreline of Puget Sound to guide the allocation of the RASA fresh groundwater discharge total ($Q_{RASA\ DD}$) to the various subbasins. This approach assumes that:

- The relative distribution of recharge in the near vicinity of the Puget Sound shoreline is an indicator of the local hydrogeologic and climatic setting. The proportion of recharge can therefore be used as a surrogate for the proportion of direct discharge likely to occur along each subbasin shoreline.
- The large proportion of the submarine groundwater discharge to Puget Sound is derived from the shallower portions of the aquifer system. Discharge from deep, regional-scale flow paths is relatively negligible.
- The annual rates of direct discharge and recharge across the study area have not changed significantly since the RASA estimates were published in 1998 (due to changes in land cover, or climatic condition).

[4] After some experimentation, a 1500-meter wide *Recharge Zone* was selected to represent the approximate portion of the study area groundwater flow field that discharges directly to Puget Sound. The total annual average volume of recharge entering a 1500-meter wide *Recharge Zone* closely approximates the upper-bound estimate of fresh groundwater discharge to the Sound reported by Vaccaro and coauthors (see Groundwater Discharge Analysis discussion section). In certain narrow-landform cases (islands, peninsulas), a *Recharge Zone* <1500 meters wide captured all recharge on the landform.

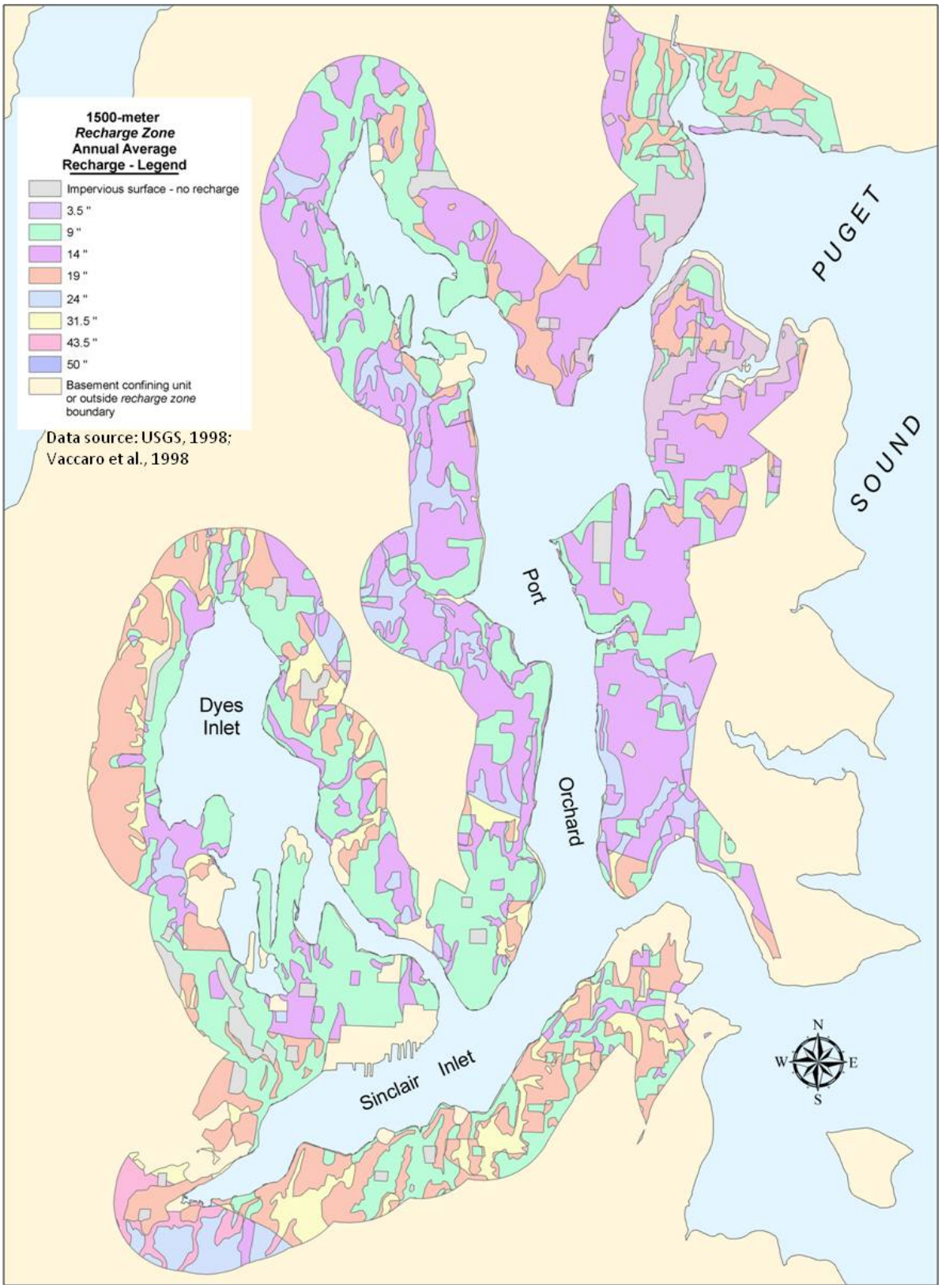

Figure 4. Example *Recharge Zone* Analysis – Sinclair/Dyes Inlet Subbasin.

No direct groundwater discharge was estimated for the portion of the Olympic Peninsula shoreline 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. The amount of submarine discharge and toxic groundwater load from this area is assumed to be negligible.

Groundwater Chemical Concentration Data

Data Sources

Estimates of the concentration of toxics in the groundwater discharge to Puget Sound (C_{COC}) were developed by compiling data from readily available sources. No new sampling was conducted for the study. Groundwater concentration data for the COCs listed in Table 1 were drawn primarily from two internet-based, regional-scale monitoring databases: (1) Ecology's Environmental Information Management (EIM) system (www.ecy.wa.gov/eim/index.htm), and (2) USGS's National Water Information System (NWIS; http://waterdata.usgs.gov/wa/nwis/nwis). Local toxics data from the King County Groundwater Database were also used for the analysis (http://green.kingcounty.gov/groundwater/default.aspx). The data queried from all of these systems were processed and analyzed using standard database, spreadsheet, and GIS software programs (e.g., Microsoft Access 2007, Microsoft Excel 2007, Esri ArcMap 9.3).

Groundwater toxics data associated with a number of contaminated facilities investigated under the authority of the U.S. Environmental Protection Agency (USEPA) *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA, a.k.a. 'Superfund') program are not currently available in a centralized, publically-accessible database. Therefore, groundwater data from CERCLA sites were not incorporated into this study's datasets.

Data Screening

The following screening steps and assumptions were employed when compiling groundwater quality data for the loading analysis:

- All sample concentrations were converted to a common concentration unit (ug/L).
- Samples that were qualified due to blank contamination concerns were omitted.
- The concentration values for results qualified as estimates (e.g. "J" qualified) were used without modification.
- Sample results older than 1990 were omitted from the loading analysis.
- In cases where there were multiple sample results for a monitoring station, the most recent result was used for the loading analysis.
- All samples were assumed to represent dissolved-phase conditions (regardless of reported filtration level).

- To best represent the quality of the water in the near vicinity of the marine boundary (and still provide a dataset large enough for the analysis), the available datasets were screened using GIS tools to select results only collected within a *Buffer Zone* extending 500 meters (1640 feet) immediately inland of the shoreline (regardless of well depth). In light of the fate and transport characteristics of the COCs listed in Table 1, it was assumed that concentrations reported from wells upgradient of the 500-meter *Buffer Zone* would not necessarily represent the water quality condition likely to ultimately arrive at the marine boundary. (See additional discussions below.)

Statistical Analysis

Key descriptive percentile statistics (10^{th} percentile, 25^{th} percentile, median) were generated for each COC in Table 1, for the *Buffer Zone* in each subbasin. No data transformation was conducted prior to calculation of the percentile statistics. Percentile statistics were not calculated in cases where there were less than 5 data values available for a parameter/subbasin combination. The rules used to extrapolate COC concentrations to areas with insufficient data are presented later in this report.

Non-Detect Substitution Rules

A significant percentage (70-100%) of the COC results for the groundwater samples used for the loading analysis were reported to be below the reporting limit of the analytical method (i.e. non-detect).[5] Since the datasets 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 used to develop concentration statistics without first substituting an assumed concentration value. A number of possible statistical substitution methods for non-detects have been suggested for this problem (e.g., US EPA, 2009). Each of these methods can introduce its own bias, 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 (or below) what actually occurs in the environment.

To address the uncertainly in the loading analysis that may result from this problem, three different non-detect substitution methods were tested for each COC dataset to evaluate the influence of the substitution approach on the loading results (similar to techniques described by Pelletier and Mohamedali, 2009).

[5] The high proportion of non-detects is probably the result of a variety of factors. These include: (1) a number of the organic COCs do not occur naturally in the groundwater environment, (2) due to their chemical properties (low solubilities and high partitioning coefficients - see Table 2), many of the COCs exhibit a strong affinity to sorb to, or associate with, the soil/sediment matrix, limiting dissolved (aqueous) phase concentrations and transport away from source areas, and (3) detection limits, particularly for older samples, may have been higher than the COC concentrations routinely occurring in the aqueous environment.

The methods include:

- Method 1 – Before calculating percentile statistics, a concentration of 0.5RL was substituted for each non-detect result, regardless of the RL concentration.
- Method 2 – Before calculating percentile statistics, a concentration equal to the lowest RL of the dataset was substituted for all non-detect results in that dataset.
- Method 3 - All non-detect results were omitted from the dataset prior to calculating percentile statistics.

Table 2. Example S, K_{ow}, K_{oc}, and K_d Values for Select COCs.

Parameter	S (mg/L)	log K_{ow} (L/kg)	K_{oc} (L/kg)	log K_d (L/kg)
Acenaphthene	2.53E+00	4.15	4.90E+03 [A]	
Acenaphthylene	2.49E+00	3.94	2.62E+03 [B]	
Anthracene	6.91E-01	4.35	2.35E+04 [A]	
Fluorene	1.34E+00	4.02	7.71E+03 [A]	
Naphthalene	1.42E+02	3.17	1.19E+03 [A]	
Benzo(a)anthracene	2.91E-02	5.52	3.58E+05 [A]	
Benzo(a)pyrene	1.04E-02	6.11	9.69E+05 [A]	
Benzo(b)fluoranthene	2.07E-02	6.11	1.23E+06 [A]	
Benzo(g,h,i)perylene	2.83E-03	6.70	5.67E+05 [B]	
Benzo(k)fluoranthene	1.08E-02	6.11	1.23E+06 [A]	
Chrysene	2.63E-02	5.52	3.98E+05 [A]	
Dibenzo(a,h)anthracene	3.30E-03	6.70	1.79E+06 [A]	
Fluoranthene	1.30E-01	4.93	4.91E+04 [A]	
Indeno(1,2,3-cd)pyrene	2.49E-03		3.47E+06 [A]	
Pyrene	2.25E-01	4.93	6.80E+04 [A]	
Bis(2-Ethylhexyl) phthalate	1.13E-03	8.39	1.11E+05 [A]	
DDD	6.76E-02	5.87	4.60E+04 [A]	
DDE			8.60E+04 [A]	
DDT	7.31E-03	6.79	6.80E+05 [A]	
Arsenic (III,V)				3.4
Cadmium(II)				2.9
Copper(II)				2.7
Lead(II)				4.1
Mercury(II)				3.8
Zinc(II)				3.1

S – Solubility, estimated with K_{ow}. Values from USEPA Risk Assessment Information System (RAIS).
Kow – Octanol/water partition coefficient. Values from USEPA Risk Assessment Information System (RAIS).
K_{oc} – Soil organic carbon-water partitioning coefficient.
[A]: Values from Ecology's Cleanup Levels and Risk Calculations (CLARC) database, https://fortress.wa.gov/ecy/clarc/CLARCHome.aspx.
[B]: Values from USEPA Risk Assessment Information System (RAIS).
log K_d – Soil-soilwater distribution coefficient. Values from USEPA (2005).

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 dataset, it is important to recognize inherent biases in the chemical data that are available. Without adjustment, these biases could distort the results of the loading analysis.

A significant majority of the data that qualified for the loading analysis were drawn from Ecology's EIM system. Given Ecology's regulatory focus[6], the groundwater toxic results in the EIM database are assumed to be biased towards (and spatially clustered at) industrial or commercial sites that are known or suspected to have point-source-related toxic contamination (Table 3). Without modification, concentration statistics developed from datasets built primarily with EIM data would likely bias the loading calculations high, since these values would mostly represent conditions beneath a comparatively small, *impacted* portion of the land adjacent to the marine shoreline.[7]

A smaller set of COC data results were available within the 500-meter-wide *Buffer Zone* from the USGS NWIS database. Although the USGS provides technical support to the Department of Defense concerning contaminated federal facilities[8], 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)(Table 3). A small number of NWIS samples specifically identified as associated with a contaminated source area (e.g., in the vicinity of the Keyport Naval Undersea Warfare Center landfill) were assumed to represent *impacted* conditions.

County-administered groundwater monitoring programs generally focus on tracking area-wide ambient conditions. In most cases, known locations of point-source contamination are deliberately avoided by local ambient monitoring programs. A small set of COC data results from the King County Groundwater Monitoring program were available within the *Buffer Zone* and were assumed to represent *ambient* conditions (Table 3).

Table 3. Summary of Chemical Data Bias Assumptions for COC Data.

EIM	NWIS	King County
Assume all data values represent *impacted* conditions	Assume all data values represent *ambient* conditions, unless specifically identified as *impacted*	Assume all data values represent *ambient* conditions

[6] For example, implementing monitoring studies in response to the Model Toxics Control Act (MTCA) or state Dangerous Waste regulations.

[7] The large number of data values involved, limited project schedule, and limited metadata associated with the monitoring results precluded an effort to specifically identify, select out, and statistically evaluate only "up-gradient" or "background" wells at contaminated facilities. Also, even within the EIM data sets, non-detects represent a large proportion of the available results.

[8] For example, military installations under investigation through the *Comprehensive Environmental Response, Compensation, and Liability Act* (Superfund) program.

Groundwater Mass-Flux Estimation Methods

To estimate an annual COC mass flux, Equation 1 requires that a value be assigned to represent the bulk dissolved-phase concentration of the COC in the groundwater discharge. Assigning a single COC concentration value to a subbasin's discharge, however, may not adequately represent variations in conditions between *impacted* and *ambient* areas, or beneath different land-use types.

To (1) adjust for the bias introduced by the large percentage of potentially *impacted* data results, (2) better reflect *ambient* conditions away from point sources of toxic contamination, and (3) represent assumed differences in *ambient* water quality condition beneath differing levels of land development, Equation 1 was modified to Equation 3:

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

where:

F_{SB} = the estimated total annual mass flux of the COC delivered to the subbasin marine boundary by direct groundwater discharge (kg/yr).

$Q_{SB\,DD}$ = the estimated groundwater discharge rate to the subbasin marine boundary (L/sec) (from Equation 2).

SL_{IMP} = the total length of subbasin shoreline classified as *impacted* (meters).

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

SL_{NUA} = the total length of subbasin shoreline classified as *non-urban-ambient* (meters).

SL_{TOT} = the total length of subbasin shoreline (meters).

C_{IMP} = the estimated COC concentration for subbasin *impacted* areas (ug/L).

C_{UA} = the estimated COC concentration for subbasin *urban-ambient* areas (ug/L).

C_{NUA} = the estimated COC concentration for subbasin *non-urban-ambient* areas (ug/L).

Figure 5 illustrates the GIS method used to map and quantify the SL_{IMP}, SL_{UA}, and SL_{NUA} values for each subbasin for each COC, guided by the data set assumptions presented in Table 3.[9] The land-use spatial data shown in Figure 6 was used to define the boundaries between urban and non-urban areas within the *Buffer Zone*.

The concentration statistics C_{IMP}, C_{UA}, and C_{NUA} were derived using the criteria outlined in Table 4. In cases where the C_{UA} and C_{NUA} concentration values were estimated using a percentile concentration of an *impacted* dataset (Table 4), the 25th and 10th percentile values of the *impacted* datasets where assumed to represent the bulk *ambient* concentrations likely occurring away from *impacted* areas, under differing levels of land development.

[9] Within a given subbasin, the total shoreline length (SL_{TOT}) is the same for all COCs. The allocation of total shoreline length to the three *impacted* or *ambient* categories (SL_{IMP}, SL_{UA}, and SL_{NUA}) varies, however, for each COC depending on data availability in the EIM database. Thus, unlike the urban/non-urban categorization illustrated on Figure 5, categorization of a shoreline as *impacted* or *ambient* is not dependent on previously mapped land-use characteristics.

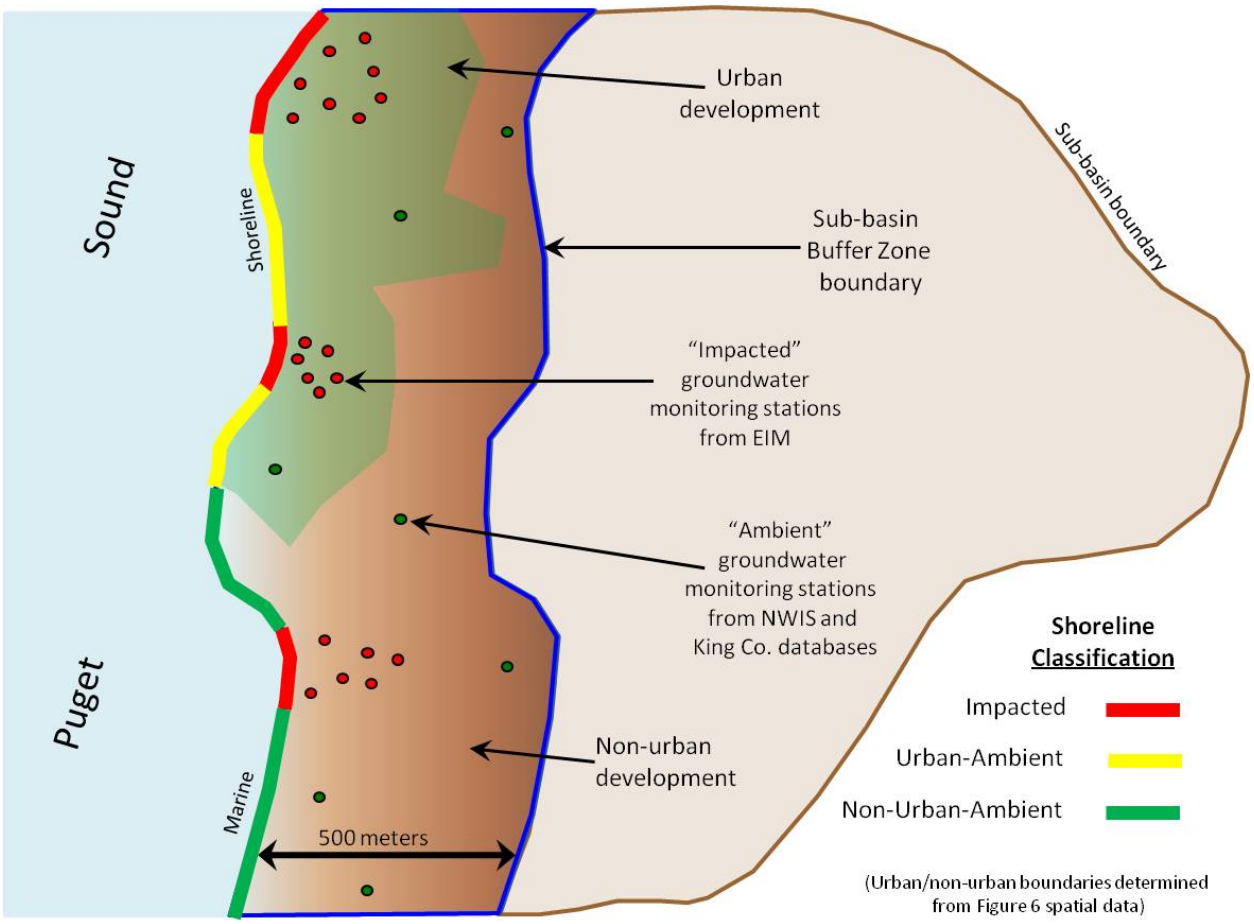

Figure 5. Schematic of Method for Classifying Shoreline Type for Loading Calculations.

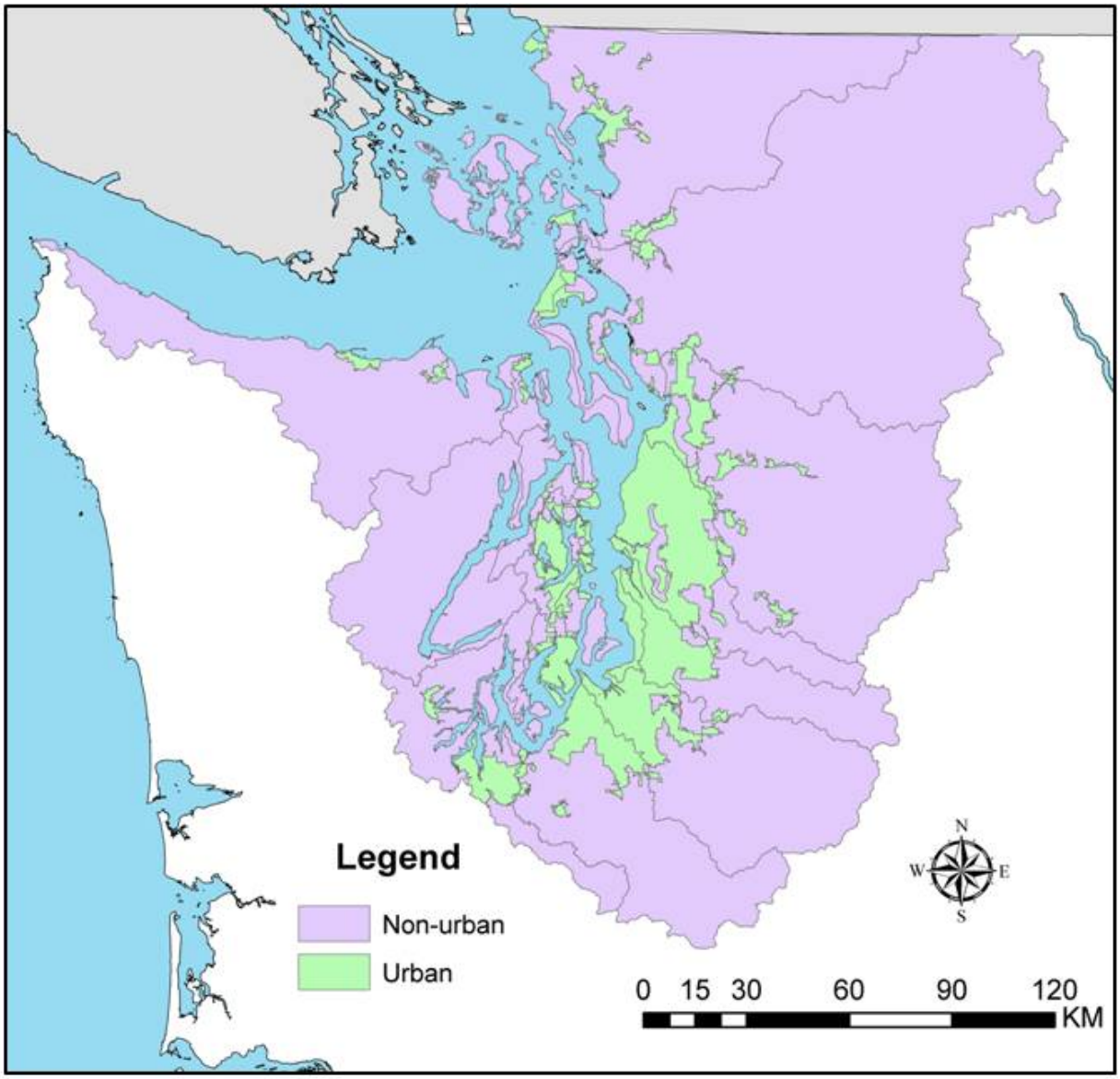

Figure 6. Urban/Non-Urban Land Use in the Puget Sound Basin.

Table 4. COC Concentration Estimation Rules.

C_{IMP}		C_{UA}		C_{NUA}	
If					
Subbasin *impacted* sample set $n \geq 5$	Subbasin *impacted* sample set $n < 5$	Subbasin *urban-ambient* sample set $n \geq 5$	Subbasin *urban-ambient* sample set $n < 5$	Subbasin *non-urban-ambient* sample set $n \geq 5$	Subbasin *non-urban-ambient* sample set $n < 5$
Then					
C_{IMP} = median of pooled subbasin *Buffer Zone impacted* sample concentrations	$C_{IMP} = 0$	C_{UA} = median of pooled subbasin *Buffer Zone urban-ambient* sample concentrations	C_{UA} = median of pooled Puget Sound-wide *Buffer Zone urban-ambient* sample concentrations, if sample set $n \geq 10$	C_{NUA} = median of pooled subbasin *Buffer Zone non-urban-ambient* sample concentrations	C_{NUA} = median of pooled Puget Sound-wide *Buffer Zone non-urban-ambient* sample concentrations, if sample set $n \geq 10$
			Otherwise		**Otherwise**
			$C_{UA} = 25^{th}$ percentile of pooled Puget Sound-wide *Buffer Zone impacted* sample concentrations, if sample set $n \geq 10$*		$C_{NUA} = 10^{th}$ percentile of pooled Puget Sound-wide *Buffer Zone impacted* sample concentrations, if sample set $n \geq 10$*

*If the pooled Puget Sound-wide *Buffer Zone impacted* sample set was n <10, no load was calculated.

Results

Shoreline Classification Analysis

Tables A-1 through A-34 (Appendix A) present the results of the GIS shoreline classification analysis for each COC/subbasin combination. Shoreline sections classified as *impacted* represent on average <1 to 10% of the study area shoreline length total (depending on COC). *Impacted* shoreline sections were co-located almost exclusively with urban development. In several of the heavily industrialized subbasins (e.g. Commencement Bay, Elliott Bay), the percentage of shoreline classified as *impacted* exceeded 50%. Shoreline sections classified as *non-urban-ambient* represent approximately two-thirds (64%) of the total study area.

Groundwater Discharge Analysis

Tables B-1 through B-34 (Appendix B) present the results of the volumetric discharge analysis for each COC/subbasin/shoreline-class combination.

On a relative basis, the majority of the groundwater volume predicted to discharge from *impacted* areas originates from the Commencement Bay, Elliott Bay, and South Sound West subbasins. Most of the discharge from *urban-ambient* areas was assigned to the South Sound East, Sinclair/Dyes Inlet, and Main Basin subbasins. The majority of discharge from *non-urban-ambient* areas was assigned to the Hood Canal South and South Sound West subbasins.

On a volumetric basis, *non-urban-ambient* areas are predicted to deliver approximately 75% of the total discharge volume, while *impacted* areas deliver approximately (~) 1% of the discharge total by volume. Using the methods and assumptions described above, over half (~55%) of the groundwater volume arriving at the Puget Sound marine boundary is predicted to originate from the three subbasins located at the southern end of the Sound: Hood Canal South, South Sound West, and South Sound East.

COC Groundwater Concentration Estimates

Non-Detect Substitution Method Evaluation

The high percentage of non-detects in nearly all of the datasets means that the choice of the value substituted for each non-detect has, as expected, a significant influence on the final concentration statistics (and in turn the mass-flux estimates). Non-detect frequencies for organic COCs were typically 80-90% of the dataset. Non-detect frequencies for inorganic COCs averaged ~70% of the dataset. The only COC with a non-detect frequency consistently less than 50% was zinc.

Concentration (and loading) estimates were ultimately developed using two of the three non-detect substitution methods evaluated (Method 1 and 2). Omitting all non-detect values prior to calculating percentile statistics (Method 3) frequently resulted in datasets with fewer than 5

values. Five samples was the minimum (n) threshold established in Table 4 for calculating sub-basin concentration statistics.

In cases where there were enough detections to calculate concentration statistics using Method 3, cumulative frequency distribution (CFD) analyses indicated the method would often bias the key concentration statistics significantly higher than the other two methods. (See example Figures 7, 8, and 9.) The Method 3 statistical results indicated representative concentration thresholds that were inconsistent with those expected for datasets with such high non-detect percentages. For these reasons, the Method 3 substitution approach was dropped from further use in the loading analysis.

In most cases, the Method 1 approach (substituting 0.5RL for all <RL values) resulted in concentration statistics that were higher than the Method 2 approach (substituting the lowest RL in the dataset for all <RL values), particularly for the median and 25th percentile values. (See example Figures 7, 8, and 10.) In select cases, however, the CFD analysis indicated that the Method 2 substitution approach produced the higher statistical values of the two methods. (See example Figures 9 and 11.) The widest variation in concentration between substitution methods was most frequently recognized for the concentration median. The spread in predicted concentration between the methods was typically narrower for the 10th and 25th percentile values.

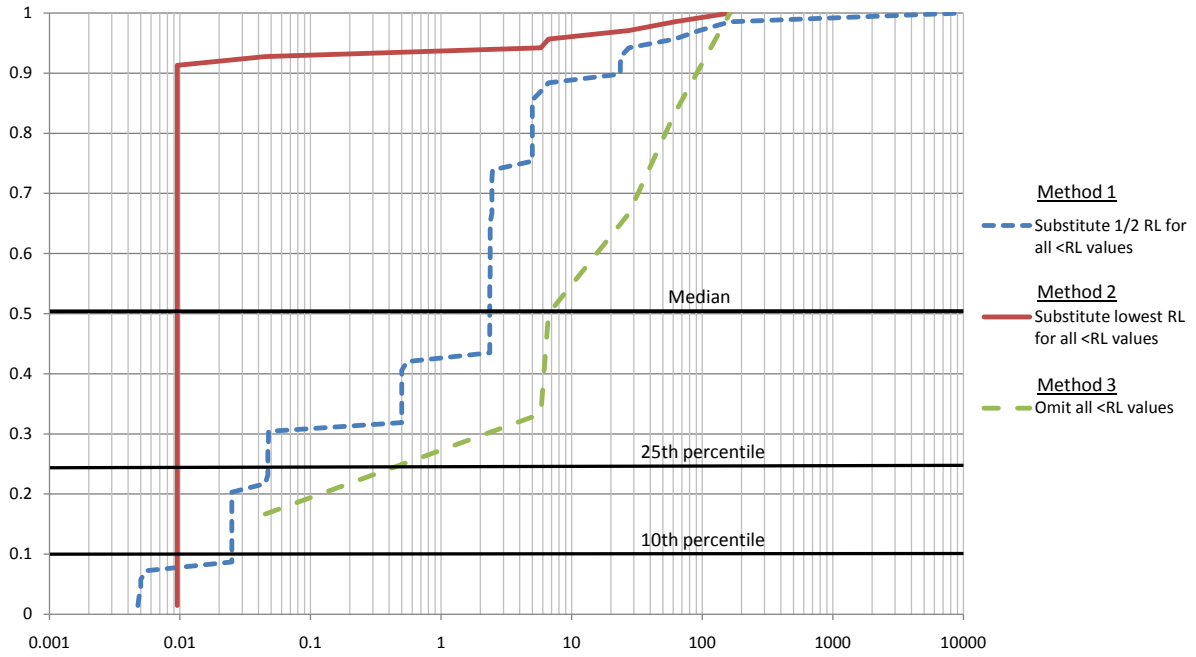

Figure 7. CFD Graph for Non-Detect Substitution Method Comparison: Port Gardner - Benzo(a)pyrene Dataset.

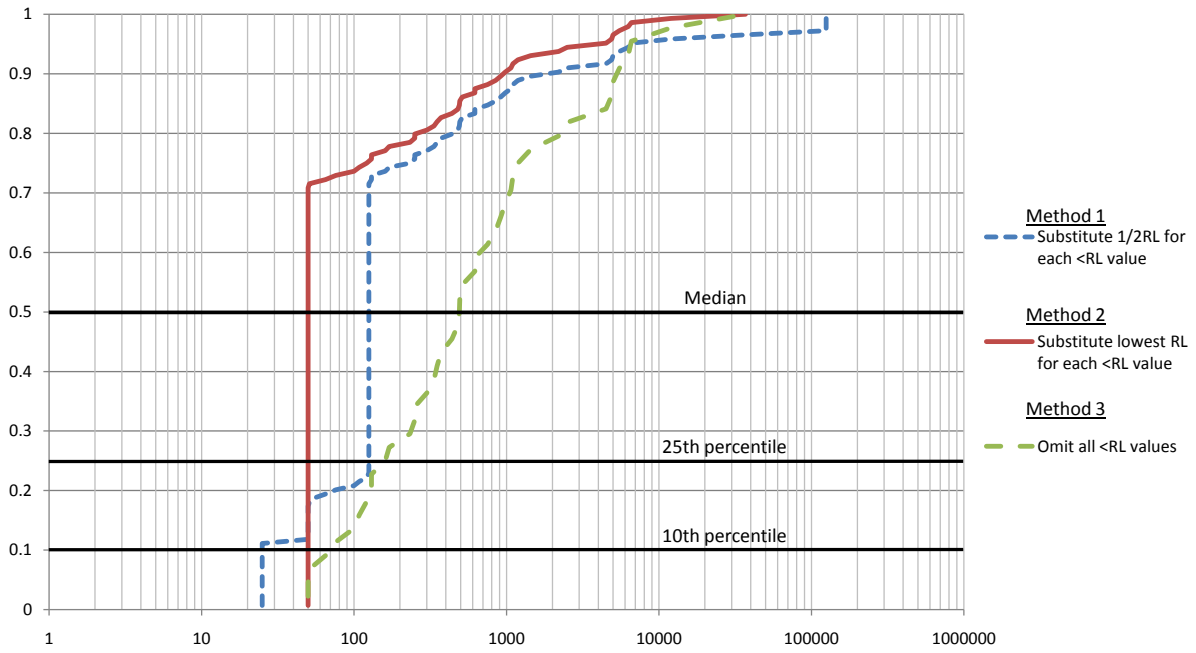

Figure 8. CFD Graph for Non-Detect Substitution Method Comparison: Elliott Bay - Gasoline Range Organics Dataset.

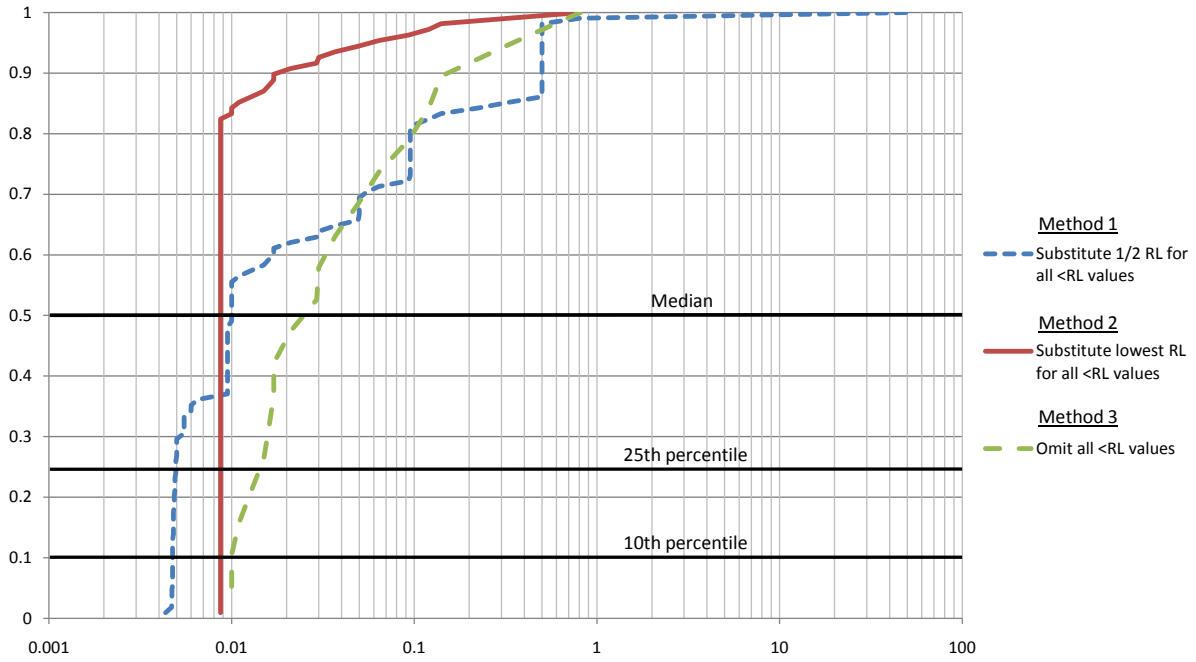

Figure 9. CFD Graph for Non-Detect Substitution Method Comparison: South Sound West - Chrysene Dataset.

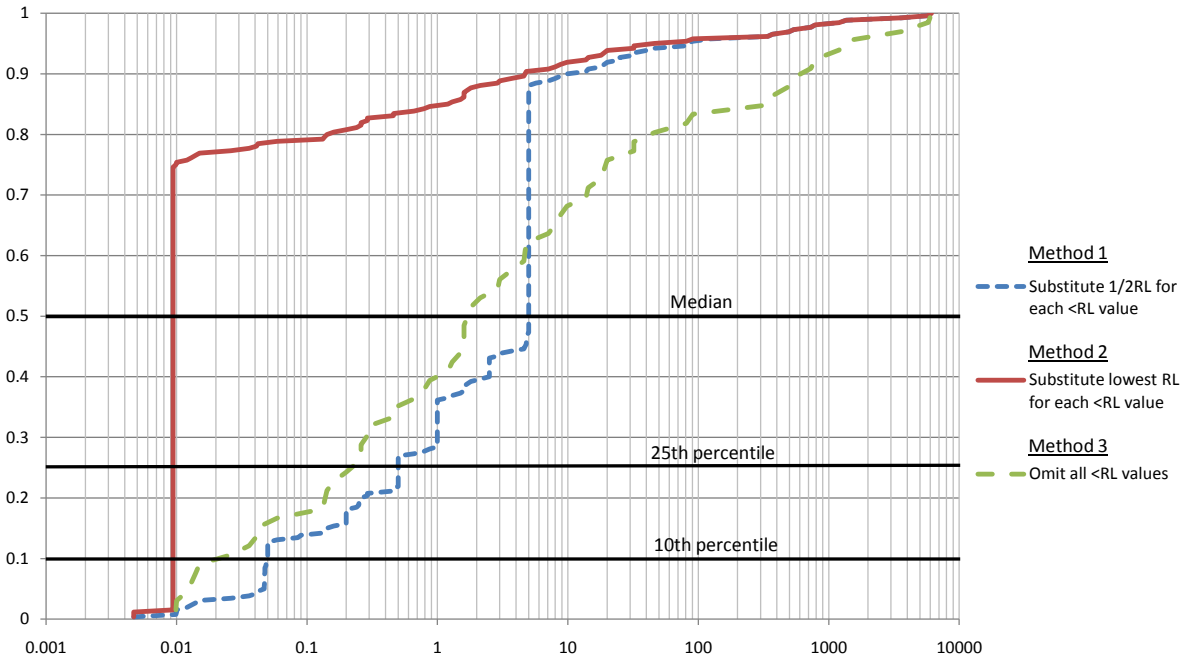

Figure 10. CFD Graph for Non-Detect Substitution Method Comparison: Commencement Bay - Naphthalene Dataset.

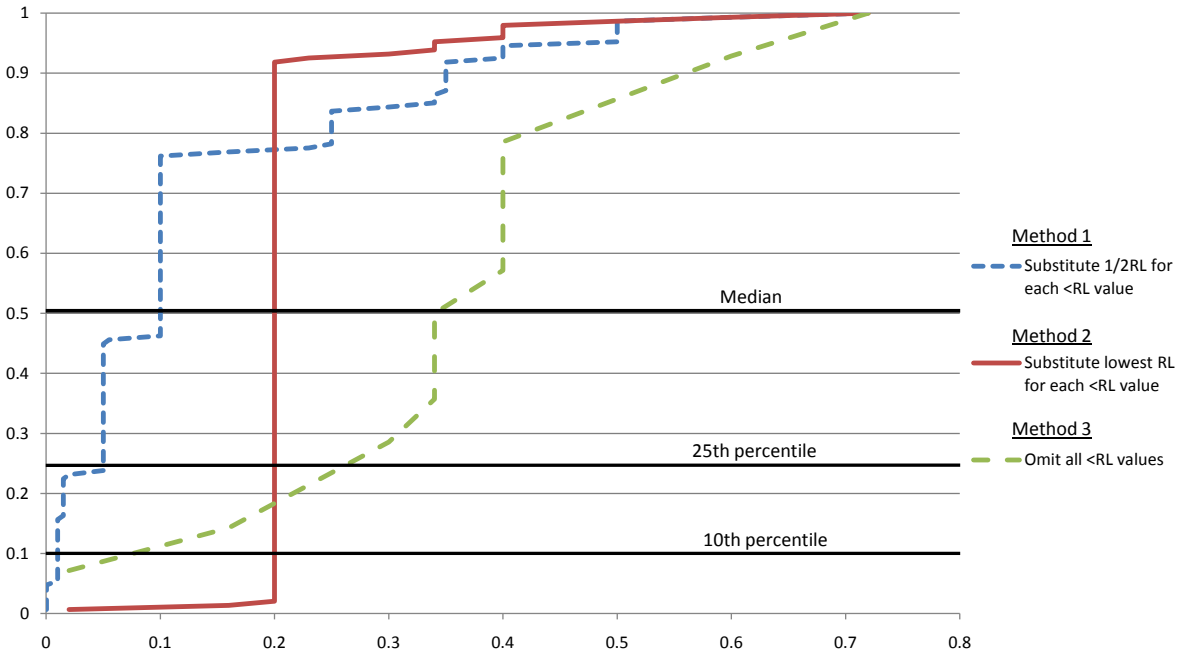

Figure 11. CFD Graph for Non-Detect Substitution Method Comparison: Commencement Bay - Mercury Dataset.

Concentration Estimates

The left-hand columns of Tables C-1 through C-34 (Appendix C) present the concentration estimates developed for each COC/subbasin/shoreline-class combination. The Appendix C table values were developed using the Method 1 non-detect substitution rule. Tables D-1 through D-34 (Appendix D) present concentration estimates using the Method 2 non-detect substitution rule. Table E-1 (Appendix E) summarizes the basis for the derivation of the C_{UA} and C_{NUA} values for each COC/subbasin combination, per the rules outlined in Table 4.

There was not sufficient data available to develop concentration or mass-flux estimates for the following parameters: triclopyr, nonylphenol, PBDEs, oil and grease, and PCBs.

Direct Groundwater Discharge COC Mass-Flux Estimates

The right-hand columns of Tables C-1 through C-34 (Appendix C) present annual mass-flux estimates for each COC, for each subbasin (F_{SB}), using the Method 1 0.5RL non-detect substitution rule. Tables D-1 through D-34 (Appendix D) present annual mass-loading estimates for each COC for each subbasin, using the Method 2 lowest RL non-detect substitution rule.

Table 5 summarizes the Puget Sound-wide annual mass-flux estimates for each COC (F_{PS} = the sum of the individual subbasin F_{SB} values). The loading summary reflects the lower- and upper-range groundwater discharge scenarios reported in the USGS RASA study water budget (low flow = 2.832E+03 L/sec, high flow = 2.832E+04 L/sec; Vaccaro et al., 1998).

With the exception of gasoline range organics and mercury, the mass-flux estimates calculated using the Method 1 non-detect substitution rule resulted in consistently higher values than the Method 2 rule. On a mass basis, the largest loads are represented by the petroleum COCs and toxic metals. Highly insoluble, strongly attenuated organic toxics such as DDTs or dioxin/furans showed significantly smaller annual loading values.

In most cases, the largest COC loads are predicted to originate from the *non-urban-ambient* areas of the basin, particularly the South Sound West and Hood Canal South subbasins. This is mostly a function of the fact that these areas deliver the highest annual groundwater volumes ($Q_{SB\,DD}$) in the study area. The exceptions (e.g. the Method 1 Commencement Bay PAH estimates) are largely a function of a C_{COC} value that was biased high by non-detect substitution.

Table 5. Estimated Annual Direct Groundwater Discharge COC Mass Flux (F_{PS}) Summary – Puget Sound Basin (kg/yr).

Parameter	Scenario: 0.5RL[A]		Scenario: Lowest RL[B]	
	Low Flow	High Flow	Low Flow	High Flow
2,4-DDD	0.02	0.22	0.04	0.43
2,4-DDE	0.02	0.22	0.04	0.43
2,4-DDT	0.02	0.22	0.04	0.43
4,4-DDD	0.18	1.8	0.04	0.43
4,4-DDE	0.31	3.1	0.04	0.44
4,4-DDT	0.17	1.7	0.04	0.45
Total DDT group (kg/yr)	**0.72**	**7.3**	**0.24**	**2.6**
Acenaphthene	1.9	19	0.27	2.7
Acenaphthylene	2.9	29	0.40	4.0
Anthracene	3.4	34	0.42	4.2
Fluorene	3.3	33	0.25	2.5
Naphthalene	16	162	5.4	54
Phenanthrene	3.4	34	0.28	2.8
Total LPAH Group (kg/yr)	**31**	**311**	**7.0**	**70**
Benz(a)anthracene	2.4	24	0.87	8.7
Benzo[a]pyrene	2.2	22	0.42	4.2
Benzo(b)fluoranthene	2.1	21	0.39	3.9
Benzo[g,h,i]perylene	2.1	21	0.41	4.1
Benzo[k]fluoranthene	2.1	21	0.38	3.8
Chrysene	2.3	23	0.31	3.1
Dibenzo[a,h]anthracene	2.7	27	1.7	17
Fluoranthene	3.1	31	0.43	4.3
Indeno[1,2,3-c,d]pyrene	2.3	23	0.87	8.7
Pyrene	3.1	31	0.41	4.1
Total HPAH Group (kg/yr)	**24**	**244**	**6.2**	**62**
Diesel Range Organics	3423	34230	1844	18441
Gasoline Range Organics	2849	28492	4469	44690
Lube Oil	6241	62409	6030	60305
Arsenic	79	794	60	602
Cadmium	43	431	12	124
Copper	427	4274	99	990
Lead	210	2096	44	438
Mercury	4.7	47	9.4	94
Zinc	1967	19672	1966	19658
Bis(2-ethylhexyl) phthalate (DEHP)	44	440	14	136
Total TCDD	0.08	0.84	0.07	0.66
Total TCDF	0.11	1.1	0.13	1.3
Triclopyr Nonylphenol Polybrominated diphenyl ethers (PBDEs) Oil and Grease Polychlorinated biphenyls (PCBs)	Insufficient Data			

[A] - Method 1: 0.5RL - One half the reporting limit was substituted for all non-detect values.
[B] - Method 2: Lowest RL - The lowest reporting limit of the data set was substituted for all non-detect values.
Low flow scenario assumes a total direct groundwater discharge rate to Puget Sound of 2832 L/sec.
High flow scenario assumes a total direct groundwater discharge rate to Puget Sound of 28320 L/sec.

Discussion

Groundwater Discharge Analysis

The loading analysis assumes that previously published values for the volume of fresh groundwater discharge to Puget Sound are valid; the estimated *total* RASA direct groundwater inflow rate to the Sound was adopted without further modification.

An analysis of the spatial distribution of near-shore recharge was used to allocate the RASA groundwater discharge total across the study area subbasins. The resulting distribution of groundwater inflow to the Sound is considered a reasonable, large-scale approximation of real world conditions. The method predicts the southern Puget Sound area as the focus of a significant percentage of the total study area discharge volume, a finding consistent with previously described regional-scale variations in precipitation, recharge, hydrogeologic setting, and subsurface hydraulic properties (Vaccaro et al., 1998).

The relative variations in the amount of groundwater discharge between subbasins are reasonably well matched with the variations in discharge magnitude predicted by the six RASA study numerical cross-section models of groundwater flow (Vaccaro et al, 1998). Although direct comparisons are complicated by differences in study area boundaries, the predicted distribution patterns and magnitudes of groundwater flow presented in this report are also consistent with other published estimates of local-scale groundwater discharge to the Sound (see Table 6). The local unit-length-groundwater-discharge rates presented in Table 6 are in some cases higher than the values averaged across Puget Sound as a whole. This is largely due to the fact that the values presented in the table are mostly for study areas located in the southern half of the Sound, where precipitation and recharge rates are higher than average.

Table 6. Unit Groundwater Discharge Estimate Comparison.

Study Area	Reference	Reported study area groundwater discharge rate to marine waters (L/sec)	Approximate length of study area marine shoreline (km)	Study area unit length groundwater discharge rate (L/sec/km)
Thurston County	Drost et al., 1999	3441	187	18.4
Chambers-Clover Creek	Savoca et al., 2010	879*	60	14.7
Navy Base Bangor	Van Heeswijk and Smith, 2002	435	62	7.0
Hood Canal	Paulson et al., 2006	7300	352	20.7
Bainbridge Island	Frans et al., 2011	391	85	4.6
South Sound West	This study	633 - 6334	437	1.4 - 14.5
South Sound East		363 - 3632	304	1.2 - 11.9
Hood Canal North		164 - 1637	143	1.1 - 11.4
Hood Canal South		574 - 5741	266	2.2 - 21.6
Sinclair/Dyes Inlet		178 - 1777	209	0.9 - 8.5
Puget Sound	Vaccaro et al., 1998	2832 - 28320	3621	0.78 - 7.8

*Assumes 10% of total reported groundwater discharge to surface water goes to marine waters.

The selection of a 1500-meter-wide *Recharge Zone* results in an annual total recharge rate (3.23E+04 L/sec) to this zone that is in close hydraulic balance with the upper-bound estimate of fresh groundwater discharge range reported by Vaccaro and co-authors (2.83E+04 L/sec). This suggests that this zone roughly approximates that portion of the Puget Sound basin that typically delivers groundwater directly to the Sound (versus baseflow to streams that discharge to the Sound).

COC Groundwater Concentration Estimates

The COC groundwater concentration estimates presented in this report were developed from data readily available to the author. There are a number of known or potential limitations within these datasets that could influence how well the values represent field conditions. In most cases, the factors that could affect data representativeness or introduce bias into the concentration results were ignored[10]; the reported sample results were assumed to represent the true subsurface condition. The limited number of sample data, particularly those collected to assess *ambient* conditions, also demanded a variety of extrapolation assumptions that can affect the accuracy of the concentration estimates. Assembling the information required to validate each of these assumptions was beyond the scope of the current project.

Due to the very high frequency of non-detects in the datasets, the rules adopted for non-detect substitution probably have the greatest influence of all factors on the final concentration statistics. In many cases, the final concentration value assigned for a parameter was simply a reflection of the detection limit distribution within the dataset. The concentration statistics generated by the Method 1 substitution approach in particular are likely biased high. For example, the use of the 0.5RL substitution approach in some cases resulted in an *ambient* concentration estimate for a non-naturally-occurring COC that was equal to or higher than the concentration established for the *impacted* areas of the same subbasin (e.g. Port Gardner lube oil).

Few published estimates for regional-scale COC concentration averages are available to provide a basis for comparison to the *ambient* values assigned for this study. Puget Sound-area groundwater data for naphthalene, arsenic, cadmium, copper, lead, and zinc were queried from the USGS National Water-Quality Assessment (NAWQA) database to provide a benchmark against which to judge the *ambient* values used for the loading analysis (USGS, 2011; Focazio et al., 1999). The NAWQA sampling stations represent both wells randomly selected throughout the Puget Sound basin, and wells specifically located beneath several major land-use classifications (e.g. urban, agricultural, mixed; see Gilliom et al., 2005). The large majority of the NAWQA wells identified for the comparison exercise are located upgradient of the 500-meter-wide *Buffer Zone* used for the loading analysis.

[10] For example: improper sample handling could bias redox sensitive species lower or higher than the actual in-situ condition; the presence of colloids or fine particles that bear sorbed or precipitated COCs could bias the analysis result high; the sampling site may have since been remediated, so the results no longer represent current conditions, etc.

Table 7 summarizes the median values calculated for the Puget Sound NAWQA COC data. All non-detect values in the NAWQA datasets were substituted using the Method 1 rule prior to calculating the median. Comparing the NAWQA medians to the *ambient* values assigned for the *urban-ambient* and *non-urban-ambient* areas indicates the loading analysis concentrations used for this study are typically equivalent to or higher than predicted by the NAWQA values. One important reason for the differences noted is the consistently lower detection limits that were used for the NAWQA sample analyses. This comparison suggests an additional reason why the COC concentrations used for the current loading analysis are assumed to represent upper-bound conditions, particularly for *ambient* areas.[11]

Table 7. NAWQA COC Data Comparison.

COC	Median concentration Puget Sound area NAWQA data[(3)] (ug/L)	NAWQA sample count/ percent non-detect	This study's average *ambient* concentration (*Urban*/*Non-urban*)[(3)] (ug/L)
Naphthalene[(1)]	0.13	145/100	0.10/0.19
Arsenic[(2)]	1.0	380/47	0.50/1.0
Cadmium[(1)]	0.02	55/36	0.50/0.46
Copper[(1)]	0.5	54/69	5.0/4.6
Lead[(1)]	0.04	54/41	5.0/1.6
Zinc[(1)]	0.9	53/0	23/22

[(1)]Data from USGS, 2011.
[(2)]Data from Focazio et al., 1999.
[(3)]Values from Appendix C. All non-detects substituted with 0.5RL.

COC Groundwater Mass-Flux Estimates

COC Transport and Attenuation

The mass-flux values calculated in this report are presented as upper-bound estimates. In addition to the use of conservative concentration statistics, the loading analysis is based on a number of simplifying assumptions about contaminant transport that introduce an additional conservative bias into the final loading values.

Although the dissolved-phase transport of a toxic contaminant in the subsurface is ultimately dictated by site-specific variations in hydrogeologic and geochemical conditions, due to their chemical properties the study COCs tend to have restricted dissolved-phase mobility in most settings (Table 2). The analysis approach nonetheless assumes that the concentration or dissolved phase mass of COCs measured within the 500-meter-wide *Buffer Zone* will not

[11] This bias in part explains why the largest COC loads are predicted to be derived from *non-urban-ambient* areas – a somewhat counterintuitive finding. The highest annual groundwater discharge volumes ($Q_{SB\,DD}$) in the study area are focused in the South Sound West and Hood Canal South sub-basins, the shorelines of which are predominantly categorized as *non-urban-ambient*. When these large volume discharges are integrated with concentration estimates that themselves are likely biased high in comparison to real field conditions (due to non-detect substitution), the resulting COC mass flux values exceed loads predicted from smaller *impacted* areas, on a mass basis.

decrease during transport to the marine boundary. In reality, a significant degree of contaminant attenuation (e.g. due to non-reversible biodegradation[12]) can occur between the point of measurement and the shoreline (Spitz and Moreno, 1996; Kresic, 2007; USEPA, 1989; Piwoni and Keeley, 1990; Riley et al., 2007).

The mass-flux estimates also only predict the maximum load likely to arrive at, but not beyond, the shoreline. In many cases there is likely additional COC attenuation/concentration reduction taking place between the shoreline and the actual point of discharge to the marine water column (which may be many meters offshore). Attenuation effects can be particularly important in the final meters of the groundwater flow path. This zone is where increased biological activity, increased organic content, and strong gradients in redox or pH condition can rapidly remove COCs from the dissolved phase prior to discharge (Ford 2005; USEPA, 2008; Beck et al., 2007; Charette and Sholkovitz, 2002; Bone et al., 2006; Jung et al., 2009). The precipitation-driven attenuation of arsenic in groundwater discharge entering the Sound from the Tacoma Asarco site due to changes in pH and redox condition is a good example of this type of COC processing (Garman et al., 2000; USEPA, 2000).[13]

There are mechanisms that can facilitate the transport of contaminants in the subsurface, accelerating the movement of normally low mobility chemicals. For instance, preferential pathways for groundwater flow may accelerate flow velocities, which in turn can limit groundwater contact times with the soil matrix, reducing opportunities for attenuation reactions to take place. In some cases geochemical reactions initiated by contact between seawater and groundwater can enhance the release of a COC from the sediment matrix, particularly for metals such as mercury and arsenic (Paulson et al., 2009; Beck, 2007; Bone et al., 2006; Liu et al., 2001). Tidal pumping effects have also been shown to speed the transfer of land-based groundwater contaminants to marine waters, although Li et al. (1999) concluded that over longer timeframes (yearly or longer), tidal pumping does not increase net mass flux.[14]

Sensitivity Analysis – Impacted Groundwater

One significant concern for this study is evaluating how well the currently available EIM data represent the true extent of near-shore groundwater that is impacted by contaminant releases. The practice of importing data to Ecology's EIM system from contamination-related investigations did not begin in earnest until approximately 2005 (Carmack, 2010). As a result, there are a number of sites located within the *Buffer Zone* with known COC groundwater contamination that do not have data currently stored in the EIM system. In addition, data from a number of contaminated sites investigated under the federal Superfund program were not readily available to include in the load calculations (e.g. the Tacoma Asarco site, the Eagle Harbor Superfund site).

[12] Adsorption processes can also significantly lower dissolved phase concentrations, but are potentially reversible.
[13] In non-destructive reactions such as the precipitation or co-precipitation of a metal, this can result in the concentration of a COC in the sediment matrix over time. Under the right geochemical conditions, such reactions can be reversible, which can result in a remobilization of the COC to the dissolved phase.
[14] Tidal pumping effects can enhance water flux, but concurrently decrease COC concentrations.

To evaluate the effect of underestimating the groundwater COC contribution to the Sound from contaminated areas, the *impacted* area mass totals in the Appendix C and D loading tables were increased by a factor of 3X. Increasing the *impacted* area mass totals by this amount tests the sensitivity of the final flux estimates to either:

1. A 3X increase in the assigned C_{IMP} concentration values in Equation 3, to evaluate the consequences of underestimating the typical severity in contamination beneath *impacted* areas, or
2. A 3X increase in the shoreline length categorized as *impacted* (SL_{IMP}) in Equation 3, to evaluate the consequences of underestimating the number and extent of contaminated sites along the Puget Sound shoreline (e.g., omitting Superfund sites).

Table 8 summarizes the results of the sensitivity test. The analysis indicates that the final mass-flux estimates are, in most cases, relatively insensitive to a 3X underestimate of the *impacted* area COC contribution. The few exceptions (Method 1 LPAH and HPAH loads), illustrate that the conservative bias introduced by the Method 1 non-detect substitution rule is further magnified by increasing the *impacted* area mass load by a factor of 3. The Method 2 values for LPAH and HPAH in this case did not show a significant increase in total load.

Table 8. Sensitivity of Puget Sound Groundwater COC Mass Flux Estimates (F_{PS}) to 3X Increase in Loading from *Impacted* Areas.

Parameter/Group	0.5RL non-detect substitution				Lowest RL non-detect substitution			
	Low Flow		High Flow		Low Flow		High Flow	
Total DDT group	0.76	+6%	7.7	+5%	0.26	+8%	2.7	+4%
Total LPAH group	54	**+74%**	540	**+74%**	7.3	+4%	73	+4%
Total HPAH group	61	**+154%**	606	**+148%**	6.4	+3%	64	+3%
Diesel Range Organics	3821	+12%	38213	+12%	2035	+10%	20254	+10%
Gasoline Range Organics	3130	+10%	31305	+10%	4638	+4%	46377	+4%
Lube Oil	6842	+10%	68423	+10%	6509	+8%	65088	+8%
Arsenic	83	+5%	833	+5%	63	+5%	629	+4%
Cadmium	45	+5%	445	+3%	13	+8%	126	+2%
Copper	431	+1%	4313	+1%	102	+3%	1015	+3%
Lead	212	+1%	2120	+1%	45	+2%	449	+3%
Mercury	4.8	+2%	48	+2%	9.5	+1%	95	+1%
Zinc	1977	1%	19765	<1%	1972	<1%	19723	<1%
DEHP	46	+5%	461	+5%	14	<1%	142	+4%
Total TCDD	0.09	+13%	0.92	+10%	0.08	+14%	0.77	+17%
Total TCDF	0.13	+18%	1.3	+18%	0.14	+8%	1.4	+8%

First value = Annual Puget Sound-wide COC mass flux in kg/yr (F_{PS}). Second value = percent increase in mass flux from Table 5.
Bolded values >20%

Conclusions

For this project, existing data sources were assembled and analyzed to estimate an upper-bound annual mass flux of toxic chemicals delivered to Puget Sound by direct (submarine) groundwater discharge. The analysis was completed for a list of 34 contaminants of concern, across 14 distinct subbasins.

The flux estimates presented are considered conservative (upper-bound). A variety of simplifying assumptions were used for the loading analysis. An evaluation of these assumptions suggests that the actual toxic loading to the Puget Sound marine boundary by direct advective groundwater transport is most likely significantly lower than estimated by this analysis.

Uncertainty in the analysis findings arises primarily from (1) the substitution assumptions used for non-detect samples and (2) limitations in the groundwater quality dataset used for calculating the loads.

The results of this study will be incorporated with loading estimates for other delivery pathways of toxic chemicals (e.g., surface runoff) during Phase 3 of the *Control of Toxic Chemicals in Puget Sound* project. This information will support ongoing efforts to improve the accuracy of the overall Puget Sound Basin toxics budget.

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On the Internet, Appendices A through E are linked to this report as separate files.