

# Western Washington NPDES Phase I Stormwater Data Characterization

# Interim Findings from 2007-2012

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## Western Washington NPDES Phase I Stormwater Data Characterization

## Interim Findings from 2007-2012

by

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# Abstract

The Washington State Department of Ecology (Ecology) conducted an interim assessment of stormwater outfall monitoring data collected by permittees as part of National Pollutant Discharge Elimination System (NPDES) Phase I Municipal Stormwater Permits. Collectively, the Phase I permittees' S8.D monitoring data represent a large, local, stormwater discharge data set unique to western Washington. Permittees monitored stormwater pollutant concentrations from four land uses (industrial, commercial, high-density residential, and low-density residential) and across seasonal and annual timeframes. All stormwater samples, except those to be analyzed for fecal coliform or total petroleum hydrocarbons, were collected using automatic composite samplers.

This project presents several methods to summarize and statistically analyze the S8.D stormwater characterization data. Approximately one-half of the permittee-collected data collected between 2007 and 2012 were provided for this project; therefore, fewer objectives were achieved such as producing loading estimates. As such, this project focused on setting up the tools and tests that will be used in the final analysis after the full data sets are provided next year. We also suggested solutions to mitigate some of the systematic problems within the current study, such as multiple reporting limits and copious volumes of non-detect data. This report discusses six valid and robust techniques to summarize results for more than 85 parameters monitored in stormwater and stormwater sediments.

Statistical summaries are provided for parameters with enough detections. Evaluations of possible correlations between the concentrations of specific pollutants in stormwater and land uses or seasons were explored. The techniques employed by this project provide an interim assessment of the baseline quality of stormwater from some Puget Sound jurisdictions.

A complete compilation of the Phase I S8.D outfall monitoring data is planned for 2014, after the final data are reported to Ecology.

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## Introduction

Stormwater transport of pollutants to receiving waters is a local and national concern. The U.S. Environmental Protection Agency (EPA) states, "*Polluted stormwater is the leading cause of impairment to the nearly 40% of surveyed U.S. waterbodies which do not meet water quality standards.*" (EPA Stormwater website). The Washington State Department of Ecology (Ecology) is authorized to administer the Clean Water Act's National Pollutant Discharge Elimination System (NPDES) permits to implement controls designed to prevent stormwater pollutants from impairing local water bodies.

Historically, our understanding and management of stormwater programs relied upon calculations based on national averages to represent local conditions. In order to understand the extent of pollutant loading by stormwater to streams, lakes, rivers, and Puget Sound, Ecology included monitoring requirements in the 2007-2012 Phase I Municipal Stormwater permit (permit)<sup>1</sup>. Ecology issued the permit to four counties, two cities, and two ports<sup>2</sup> (Ecology, 2007). Special Condition 8 (S8) of the permit consisted of three main monitoring elements:

- Stormwater outfall monitoring (S8.D).
- Targeted stormwater management program effectiveness monitoring (S8.F).
- Stormwater treatment and hydrologic best management practices (BMP) evaluation monitoring (S8.E).

This report summarizes the S8.D outfall characterization monitoring, and not the other monitoring elements.

Collectively, the Phase I Permit's S8.D stormwater monitoring data represents the largest local data set to characterize municipal stormwater discharge quality. To gain an appreciation of the potential size of the data set, a hypothetical but plausible scenario is used. If each of the six city/county permittees monitored 11 storms each year for three years at three different stormwater subbasins, then 594 storms would have been monitored. This estimate does not include the monitoring by the two ports, which monitored 11 storms each year for three years at one stormwater subbasin (66 storms). In total, the data set would potentially consist of 660 monitored storm events.

Compilation and analysis of the stormwater data as collected under S8.D of the Phase I Permit will help fill a data gap identified by a receiving water study: *Control of Toxic Chemicals in Puget Sound: Phase 3 Data and Load Estimates* by Herrera Environmental Consultants, Inc. (Herrera, 2011). This study (herein called the *Toxics in Surface Runoff Study*) has an Ecology website. The effort was part of a larger toxic chemicals assessment of pollutant loads to Puget Sound and identified stormwater as the largest pathway for toxic chemicals to enter Puget Sound. The study stated the major data gap was in regional stormwater quality information from conveyance systems and direct discharges to Puget Sound.

<sup>&</sup>lt;sup>1</sup> The 2012-2013 Phase I Municipal Stormwater Permit continued the 2007 permit's monitoring requirements, clarifying end points for these monitoring programs and requirements for data submission.

<sup>&</sup>lt;sup>2</sup> The Phase I Municipal Stormwater Permit also covers Secondary Permittees which were not required to conduct the monitoring discussed in this report.

This project provides the only known combined data assessment of direct stormwater discharge monitoring data collected in Washington. Despite capturing only one-half the data gathered under the permit, this project summarizes a substantial data set, with approximately five times more captured storm events than are in the 2011 *Toxics in Surface Runoff Study*.

## Purpose

Stormwater pollutant discharge characterization by land use on a regional scale is an Ecology priority. Stormwater management solutions and decisions are based on knowledge gathered from monitoring the types of pollutants in populated industrial, residential, and commercial land use areas. The National Estuary Program (NEP) also identified stormwater outfall characterization as a priority; it provided grant funding to Ecology to compile and review the S8.D monitoring data collected from 2007 through 2012. This project supports the original intent of the Phase I Permit by establishing a regional baseline based on monitoring results (Ecology, 2006). This report will assist stormwater managers by identifying parameters or techniques that are not effective in gaining information. This report represents an interim assessment based on the early years of the permittees' monitoring data. Some permittees are still monitoring under S8.D.

Results from this project will be useful in identifying the quality of stormwater discharge in Western Washington, which in turn will help decrease our reliance on national studies that may not be representative of western Washington's climate or land uses. Improved confidence in local stormwater event concentrations is useful for stormwater managers, regulators, treatment technology development, and future contaminant studies (e.g., source identification and loading studies).

The original intent of this project was also to calculate loads using the permittees' data (Lubliner, 2012). Since little permittee flow information was available to the author at the time of this project, load calculations were not possible. Ecology anticipates Phase I permittees will complete their submissions in Ecology's Environmental Information Management (EIM) database in 2014.

## **Permit-Defined Stormwater Monitoring**

### Monitoring Timeline

In 2009 permittees were given the option of collaborating together on monitoring. If they chose to collaborate on monitoring, they were given an extension on the compliance schedule. Table 1 shows the permittees that are monitoring only their individual jurisdiction and those that collaborated on monitoring. Figure 1 shows the timeline of stormwater monitoring and data reporting to Ecology.

#### Table 1. Lists of permittees.



### Figure 1. Timeline of Phase I permittee data submittals.

### Stormwater Monitoring Design

#### **Stormwater Monitoring**

Monitoring was conducted under Quality Assurance (QA) Project Plans written by the permittees and approved by Ecology. The monitoring program for each permittee is described in great detail in the permittees' QA Project Plans (referenced in Appendix A and available from the permittees). A few aspects of the monitoring programs are important for understanding the monitoring results presented here. The permit called for stormwater monitoring for a total of three years of data collection for each permittee under S8.D.

#### Site Selection for Outfall Characterization

The permit instructed permittees to monitor land uses where, ideally, the drainage area would constitute  $\geq 80\%$  of a particular land use. However, Ecology and the permittees found that stormwater sub-basins tended to contain more variety of land uses and meeting this 80% goal was not possible in all circumstances. Permittees monitored one location for each different land use type. The land use types monitored by permittees are:

- Counties: commercial, low-density residential, and high-density residential.
- Cities: commercial, high-density residential, and industrial.
- Ports: commercial.

In order to successfully implement the monitoring program, the site selection process had to take a number of additional factors into consideration, including access, ability to install and protect sampling equipment, flow characteristics, and tidal influence. It is important to note that not all selected monitoring locations were outfalls to receiving waters; in many cases, the monitoring location was a catch basin or other node in the system that met the project needs.

Table 2 shows the land use characterization of the drainage areas monitored by each permittee and lists the total impervious area (TIA) estimated in each of the stormwater subbasins monitored. Because estimates of effective impervious area (e.g., impervious surfaces that are connected via sheet flow or discrete conveyance) are not available, the TIA information is intended to provide some context for how much land area may be available for dispersion to the ground surface. It is important to note that given the configuration of the port properties, both ports monitored locations representative primarily of parking lot runoff.

	Land Use			
Permittee	Low-Density Residential	High-Density Residential	Commercial	Industrial
Clark County	43 acres 100% residential 7% TIA	239 acres 99% residential 1% open space 52% TIA	27 acres 83% commercial 17% residential 76% TIA	NA
Pierce County	219 acres 43% residential 55% open space 2% other 5% TIA	125 acres 62% residential 16% commercial 14% roadway 8% open space 28% TIA	11 acres 96% commercial 4% open space 96% TIA	NA
City of Tacoma	NA	1821 acres 80% residential 19% commercial 5% open space 0.8% industrial 42% TIA	181 acres 97% commercial 3% residential 65% TIA	36 acres 15% commercial 85% residential 90% TIA
Port of Tacoma	NA	NA	1.3 acres 100% commercial 82% TIA	NA
King County	43 acres 100% residential 17% TIA	5 acres 100% residential 50% TIA	5 acres 80% commercial 20% residential 80% TIA	NA
City of Seattle	NA	85 acres 95% residential 5% commercial 50% TIA	<ul><li>152 acres</li><li>61% commercial</li><li>37% residential</li><li>2% open space</li><li>61% TIA</li></ul>	<ul><li>137 acres</li><li>37% industrial</li><li>32% residential</li><li>18% open space</li><li>13% commercial</li><li>51% TIA</li></ul>
Port of Seattle	NA	NA	1.3 acres 100% commercial 95% TIA	NA
Snohomish County	68 acres 85% residential 15% school 26% TIA	20 acres 100 residential 40% TIA	34 acres 100% commercial 77% TIA	NA

 Table 2. Phase I S8.D sites and land use summary.

NA: Not applicable TIA: Total impervious area

### Storm-Event Criteria and Frequency

The permit specified the qualifying rainfall, antecedent dry period, or inter-event dry periods to define a storm event. Ecology's criteria were highly specific and necessary to ensure consistent sampling in a regional program, particularly when considering the Pacific Northwest's winter climate with constant and sometimes overlapping wet weather patterns. Qualifying storm events were defined for the wet and dry season as follows:

All Storms

- Rainfall depth: 0.2 inch minimum, no maximum
- Rainfall duration: no fixed minimum or maximum
- Inter-event dry period: 6 hours

Wet Season (October 1 through April 30)

• Antecedent dry period:  $\leq 0.02$  inch rain in the previous 24 hours

Dry season (May 1 through September 30)

• Antecedent dry period:  $\leq 0.02$  inch rain in the previous 72 hours

Ecology specified the storm-event minimum size to establish consistent sampling "Go" decisions. Permittees were required to monitor 67% of the forecasted qualifying storm events up to a maximum of 11 storms per water year. The goal was to distribute sampling across the year with 60-80% of the storms sampled in the wet season and 20-40% in the dry season. If, for a variety of reasons and despite good faith efforts, 11 "qualifying" storms were not sampled in a given year, the permittees could submit data from three storms that were "non-qualifying" for the 0.2 inch rainfall depth.

The primary reason permittees would have captured non-qualifying stormwater samples was that the storm event might not have produced the required rainfall prior to the "Go" decision to sample. Permittees made considerable efforts to mobilize and sample before learning if the storm event qualified with the permit criteria. The permit capped the number of attempts to monitor 14 storm events per year, due to this difficulty. Permittee information on timing of sampling or logistics in relation to storms was not evaluated in this project. Non-qualifying, storm-event data are included in this project summary and are not differentially treated. In this interim report there is no distinction made in the data from qualifying or non-qualifying stormevent data.

### Parameters

Parameters, the constituents measured in samples, were specified by the permit in both S8.D and Appendix 9 of the permit and were prioritized for each land use when the sample volume was limited. Table 3 lists the water quality parameters monitored in stormwater.

#### Sample Collection

Sampling methodology is described in much greater site-specific detail in each of the permittees' QA Project Plans. A brief description is provided for a basic understanding of the sample collection methodology.

For the vast majority of the parameters, the permit required stormwater samples to be collected using flow-weighted composite sampling techniques that employ automatic samplers. The flow-weighted composite sample represents the storm event's concentration for each parameter. A few parameters (e.g., fecal coliform bacteria and total petroleum hydrocarbons) were required to be collected as grab samples. Flow-weighted stormwater samples were collected by automatic samplers (such as ISCO samplers), which were triggered to begin sampling once either the rainfall criteria of 0.02" of rainfall or a presence of flow in the conduit was detected. Telecommunications to the monitoring staff from the automated equipment ensured proper sample collection. A qualifying flow-weighted composite sample was required to be collected over 75% of the storm-event hydrograph. For example, the flow-weighted composite sample represented individual aliquots taken during 18 of the first 24 hours of the storm-event hydrograph. The composite sample was defined as at least ten aliquots; but as few as seven aliquots were accepted if all other criteria were met. Analytical results from this monitoring program are thus representative of event mean concentrations (EMCs), better indicating the quality of the discharge over the length of a storm.

Precipitation and flow volume data for each storm event were also monitored in real-time via electronic sensors.

## Stormwater Sediment Monitoring Design

Entrained stormwater solids and sediments (storm sediment) samples were collected annually as grab samples. The permit recommended that the sediment sampling protocol use inline traps or other similar collection system. The list of parameters monitored in the stormwater sediment matrix only (Table 3) contained some conventional parameters, PCBs (Aroclors), and phenols.

The collection methods are known to have varied from stormwater solids sampling via in-line sediment traps. Others collected grab samples of in-water sediment or solids that had settled in catch basins. Monitoring in-line stormwater solids using traps can be unpredictable and requires long periods of submersion to adequately trap sediments. Permittees may also have treated samples differently following collection. Some may have decanted water off prior to laboratory analysis, whereas some may not have. Uncertainty is higher for sediment data in general due to the lack of defined protocols for collection and post-collection processing.

For the purposes of this interim data summary, the annual sediment samples are presumed to be comparable, and all results are compiled and evaluated. All sediment results are reported as dry weight.

Hydrology		
Storm-Event Precipitation		
Storm-Event Flow Volume		
Sampling-Event Flow Volume		
Water Quality	D = et eni e	One miles
Conventional Parameters	Bacteria	Organics DALL <sup>(a)</sup>
Turbidity	Fecal conform	PAHS <sup>(b)</sup>
Conductivity	Metals (dissolved and total)	Pesticides: Nitrogen (Prometon)
Chloride	Zinc	Pesticides: Organophosphates (Diazinon)
BOD <sub>5</sub>	Lead	Herbicides: (2,4-D, MCPP, Triclopyr,
Particle Size Distribution	Copper	Dichlobenil, Pentachlorophenol)
Grain Size	Cadmium	_
pH	Mercury	Petroleum Hydrocarbons
Hardness as CaCO <sub>3</sub>		NWTPH-Dx
Methylene Blue Activated		NWTPH-Gx
Substances (MBAS)		
Nutrients		
Total phosphorus		
Ortho-phosphate as P		
Total kjeldahl nitrogen		
Nitrite-Nitrate as N		
Sediment Quality		
Conventional Parameters	Metals	Organics
Total Solids <sup>(*)</sup>	Zinc	PAHs <sup>(a)</sup>
Total Organic Carbon	Lead	Phthalates <sup>(b)</sup>
Grain size	Copper	Phenolics <sup>(*)</sup>
Total Phosphorus	Cadmium	PCB Arociors
Total Volatile Solids	Mercury	Pentachiorophenol
		Diazinon
		Chlorpyrifos and Malathion
		Petroleum Hydrocarbons
		NWTPH-Dx

#### Table 3. Permittee-monitored parameters.

(a) PAH compounds include at a minimum but are not limited to: 1-methylnaphthalene, 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo[b]fluoranthene, benzo(k)fluoranthene, benzo[ghi]perylene, benzo(a)pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene.

(b) Phthalates include at a minimum, but are not limited to: bis(2-ethylhexyl)phthalate, butyl benzyl phthalate, di-N-butyl phthalate, diethyl phthalate, dimethyl phthalate, and di-n-octyl phthalate.

(c) Appendix 9 of the 2007-2012 and 2012-2013 permits mistakenly called for "Total Solids" when it should have said "Percent Solids" in the sediment parameter list. Despite the error in the text, this parameter was correctly analyzed by laboratories as the percent of the sediment sample that is the solid material (as opposed to water).

(d) Phenolics include but are not limited to: 2-methylphenol, 4-methylphenol, 2,4-dimethylphenol, and pentachlorophenol

### Laboratory Analytical Methods

Appendix 9 of the 2007 and 2012 Phase I Permit specified analytical methods and reporting-limit targets for each parameter. In some cases, it allowed multiple methods (believed to be comparable) to be used for analysis of a parameter, provided the reporting-limit target could be met. For example, conductivity could be analyzed using SM 2510 or EPA Method 120.1. Permittees used nine laboratories for analysis; no permittee used only a single laboratory for all parameters. Appendix B summarized the methods used for each parameter. All data for a given parameter, except total petroleum hydrocarbon (TPH) which is discussed in the *Methods* section, are pooled for analysis regardless of laboratory analytical method.

### Laboratory Quality Assurance

Each permittee's QA Project Plan was approved by Ecology, and contains sections outlining the QA process and quality control (QC) for their stormwater monitoring program. QA is a decision-making process, based on all available information that determines whether the data are usable for all intended purposes (Lombard and Kirchmer, 2004). QC refers to a set of standard operating procedures for the field and laboratory that are used to evaluate and control the accuracy of measurement data. Determination of laboratory QC and the overall stormwater monitoring program QA was performed by each permittee, per their monitoring QA Project Plans.

For this data analysis project, data entered into the EIM database or sent to Ecology in an electronic format were believed to be usable for the purposes collected under the permittees' QA Project Plans. This assumption is consistent with the QA Project Plan for this project (Lubliner, 2012).

### **Quantitation and Reporting Limits**

Ecology set reporting-limit targets in the permit to ensure the stormwater data under this monitoring program were analyzed to a consistent and comparable rigor among the various laboratories used. Reporting limits lower than those specified in the permit were allowed, provided that permittees' QCs were met and their instrumentation allowed them to resolve the parameter at a lower limit. Reporting limit and method detection limit terminology are further described below and illustrated in Figure 2. The permit did not effectively address data analysis. However, the permit's Appendix 9 listed reporting-limit targets for each parameter, and stated in the footnote:

"All results below reporting limits should be reported and identified as such. These results may be used in the statistical evaluations."

It is Ecology's expectation that the detected concentrations below the reporting limit are quantified and flagged as an estimate (e.g., typically a "J" flag).



Figure 2. Simplified diagram of laboratory thresholds and data results.

## Qualified Data

Data verification is the process of evaluating the completeness, correctness and conformance/compliance of specific data set against the laboratory method and study QA objectives. Data verification applies to activities in the field, at the laboratory, and the data user's (permittee's) review. Both the laboratory and the permittee's reviews determine whether the data record is usable as is or requires a corrective action, re-analysis, or flag to indicate qualification as estimate (J flag) or is rejected and is unusable (R or REJ flag). (J) flags may be given at the laboratory due to a slightly out of range QC sample or by the data QA managers (within the permittees' monitoring programs).

- *Method Detection Limit* The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDL is determined using the procedure at 40 CFR 136, Appendix B. The permit did not specify MDLs.
- *Reporting Limit* The reporting limit has multiple definitions and values, because it is a userdefined value imposed upon the reporting laboratory. The reporting limit may vary based on the purpose and use of the data and always should be based on statistical rigor at each laboratory. Analyte detections between the MDL and the reporting limit are reported as having estimated concentrations.

### Variation in Reporting Limits

Permittees' results had highly variable reporting limits, both between samples and between laboratories. Some variability is common and expected. Generally, the permittees' reporting limits were within the ranges or limits listed in Appendix 9 of the permit.

Figure 3 shows an example of the variability in the reporting limits for some of the non-detected compounds. This type of plot was constructed for every parameter with non-detect data. The bars represent the non-detect value (which is unknown) as extending from "zero" up to the threshold reported for each laboratory. This threshold may be the MDL or the reporting limit (RL), and this is currently unknown for this project. Ecology believes that, based on the data

gathered for this report, there may be differences where laboratories reported the detection threshold. Below the figure is a color key associated with each of the laboratories contributing to the data. In this example, dichlobenil (an herbicide) has 359 storm-event concentration records in this interim database, but more than 200 of those records are non-detects that are reported at approximately 20 different reporting limits spanning two orders of magnitude. The Permit gave a target reporting limit of 0.01 - 1.0 ug/L for dichlobenil and other pesticides.



Figure 3. The numerous non-detect reporting limits for dichlobenil.

Non-detect data are shown in these plots as line segments extending from zero to the laboratory reporting level. The color of the line segment indicates which laboratory performed the analysis. Laboratory names were removed and represented by a number. The focus of this plot is not to identify permittees or their laboratories, but rather to illustrate the number of laboratories and the numerous reporting limits reported.

There are several reasons reporting limits vary. The first relates to sample volume. The sample volume typically required for analysis has a predictable error rate associated with the analysis. When a smaller than normal volume is analyzed, the standard error increases, which in turn increases the reporting limit. The anticipated stormwater volume was difficult to predict, dependent upon the climatic event, and constrained by the capacity of the compositors. As a result some samples were likely sent to the laboratory with less than ideal volumes.

The second reason is that the sample may contain compounds that interfere with the analyses (also called *interfering matrix*). Stormwater samples, in particular, are problematic because some samples are dirty. They can contain debris, sediment, oil and other compounds that can interfere with sensitive analytical equipment. Other samples are fairly clean, depending on intensity of the rainfall or land use activities. Laboratories must clean up dirty samples prior to analyzing for the contaminant of interest. This often results in loss of resolution at low levels and in turn elevates the reporting limit.

A third reason exists for many of the organic chemistry compounds measured by EPA Method 8270D, which is a performance-based method. Performance-based methods typically have more variability in the reporting limits and more qualified data due to the matrix, interfering compounds and sample size. In many cases this variability is anticipated and is not necessarily a reflection on the quality of the laboratory's analysis.

Natural variability of concentrations in stormwater samples is also typical, and concentrations range more widely (higher and lower) than observed in surface waters or wastewater. Variability is due to numerous factors such as rainfall intensity, season, land uses, sampling bias towards first flush or not. For example, the requirement to pace the aliquot sampling to collect 75% of the storm required manual compositing and may have elevated the risk for contamination or sample loss.

Permittees are required to conduct QC and QA reviews on reported data. Because data verification was performed by the permittees, the data received by Ecology are believed to be usable. For this report, Ecology used the data as reported and did not conduct additional QA review. Rejected records were not requested and, if supplied, were not used for summary statistics.

## **Methods**

## **Data Compilation and Management**

### **Data Collection**

Permittees submitted annual monitoring reports to Ecology throughout program implementation. These reports, however, did not contain the data in an electronic format that could be readily used for this interim data assessment project. Ecology contacted the Phase I permittees in the fall of 2012 to request electronic data sent for analysis under this National Estuary Program (NEP) grant project. This report is based on permittee data available from Ecology's EIM database, or otherwise provided in electronic format, as of November 19, 2012.

Many permittees have entered more data into EIM since November 2012. Ecology expects to have all data in EIM by March 2014. A final analysis, which includes all data collected under the 2007-2013 S8.D stormwater characterization monitoring program, is planned to be completed in 2014.

Table 4 lists the period of record of the electronic data gathered for this analysis. Based on the number of permittees and period of record represented in this data set (as compared to the total permit requirement), this interim data set is estimated to be about half complete. It is important to note that some of the data used for this interim assessment may be subject to change for the final assessment, due to recent EIM submissions.

Permittee	EIM Study ID	Data Source November 2012	Period of Record
Snohomish County	WAR044502_S8.D	EIM	2009-2012
King County	NA	Not represented	NA
Pierce County	NA	Not represented	NA
Clark County	NA	Emailed*	2009-2012
City of Seattle	WAR044503_S8.D	EIM	2009-2011
City of Tacoma	NA	Emailed*	2009-2012
Port of Seattle	WAR044701_S8.D	EIM	2009
Port of Tacoma	WAR-04-4200_S8.D	Not represented	NA

 Table 4. Permittee data compiled for this report.

NA: not applicable

\* Emailed to the author

This interim assessment does not contain data from King or Pierce Counties or Port of Tacoma.

### Data Compilation and Complications

Ecology compiled the stormwater characterization data received from the permittees into a single Excel spreadsheet. Much organization was required to compile the data into a similar format using the same names (e.g. parameters and sample fraction). This was done by creating a template of column headers and transferring the permittees' data to fit the template. The transferred data were saved and, using Excel's sort and filter functions, were verified against the original file. The transferred data from each permittee were combined into a master Excel file, which served as the interim database.

Data organizational steps:

- 1. Data received from permittees either via EIM or e-mail.
- 2. Template created.
- 3. Permittees' data transferred to template.
- 4. Transferred data verified against original file.
- 5. Transferred data compiled into master Excel file.
- 6. Master Excel file analyzed.

Different laboratories used slightly different naming conventions, or reported data in different units. These types of formatting corrections had to be resolved for subsequent database queries. Table 5 provides summary formatting steps taken to combine the discordant data into a single database. Most of these steps will be unnecessary for the final report, because all the data will come from EIM and therefore be similarly named and formatted.

Organizational Steps	Example Issues	Initial Form	Final Form
Re-arrange columns to fit template arrangement	Downloaded data from EIM served as the template source.	Directly emailed data typically had less information on each sample than data from EIM	Interim data set is slightly hodgepodge looking. It preserves directly emailed data information in some custom columns.
Removed extra parameters	Laboratory control samples, surrogates, or calculated sums	<ul><li>Examples of removed</li><li>parameters include:</li><li>1. Maximum conductivity</li><li>2. Total PAHs</li><li>3. Ammonia</li></ul>	NA
Parameter names	Different laboratories use slightly different naming conventions and for the database queries; these had to be resolved in the database.	Approximately 25 names were resolved. Example: Triclopyr Trichlopyr Triclopyr (Garlon)	Triclopyr was the chosen parameter name for the database. See Table 3 for list of parameters in this interim database.
Specific parameter issues (two examples)	NWTPH-Dx Multiple products can be reported.	No guidance was given for reporting.	Sums for several categories created. See description below.
	Percent Solids was erroneously named as Total Solids in permit. Total Solids refers to a water measurement, not solids.	Most of the data were labeled Total Solids	Left as Total Solids, but is believed to be Percent Solids because the sample matrix is sediment for all data points.
Units for parameters	Laboratories and permittees reported using equivalent but different units due to the methods.	<ul> <li>Example:</li> <li>1. Fecal coliform MPN/100 mL or cfu/100 mL</li> <li>2. ug/L or ng/L or mg/L</li> </ul>	Units were preserved as sent in one column and a lookup table used to create new columns with data in one unit per parameter for graphing and statistics analysis. Fecal coliform units were assumed to be equivalent.
Sample fraction	Dissolved, total, or total recoverable. Labs used total and total recoverable interchangeably.	There were many blanks in these fields which needed to be populated for database.	Sample fraction for metals was understood to be totals if blank. The terms <i>Total</i> and <i>Total Recoverable</i> are interchangeable for NPDES program (EPA, 1998).

 Table 5. Summary of some organizational considerations for database.

### Petroleum Hydrocarbon Summation

The petroleum parameters required extra work to format results in a comprehensive manner. Petroleum hydrocarbons in stormwater were monitored using an Ecology laboratory method called NWTPH (Northwest Total Petroleum Hydrocarbon; herein called *TPH*) developed in the late 1990s (Ecology, 1997).

TPH-Gx, also called gasoline range hydrocarbon method, is the qualitative and quantitative method (extended) for volatile ("gasoline") petroleum products in soil and water. Six chromatograms identified by this method include:

- Gasoline
- Weathered gasoline
- Naphtha
- Mineral spirits #1, #2, and #3

TPH-Dx, also called diesel range hydrocarbon method, is the qualitative and quantitative method (extended) for semi-volatile (diesel) petroleum products in soil and water. There are 24 different chromatograms can be identified by this method, including:

- Jet fuels
- Kerosene
- Diesel fuel
- Diesel oils

- Hydraulic fluids
- Mineral oils
- Lubricating oils
- Fuel oils

According to the method guidance, these TPH methods were supposed to be summed into a single TPH value that is often used for compliance monitoring. Unfortunately, many of the permittees' results were reported in partial-sum categories typically used at the laboratories. For example, TPH-Dx was reported not by a sum total but as sub-categories, such as "residual range organics", or "heavy fuel oil".

Ecology determined the best path forward for these interim results was to rename obvious and similar results, preserve the partial-sum designations, and develop a summation plan for the final report. These interim assessments on the summed TPH-Gx fractions (gasoline, naphtha and mineral spirits) are called Gasoline Range Hydrocarbons.

For TPH-Dx results are presented in five sub-categories: Diesel Range Hydrocarbons, Heavy Oil Range Hydrocarbons, Heavy Fuel Oil, Lube Oil, and Motor Oil. These partial summarizations will be limited to these interim findings, because they are believed to be arbitrarily determined by each laboratory and consistency in the terms is not verified or supported by Ecology at this time (Bob Carroll and Pete Kmet, personal communication).

## **Data Analysis**

### **Computational Tools**

Microsoft Office products (Excel, Word and Access) were used in this project to sort, store, and compile the data set (Microsoft, 2007). Summary data were not corrected for significant digits in this interim assessment.

The free and open source software program "R" (<u>www.r-project.org</u>) was used to conduct tabular, graphical, and statistical analyses on this interim data set (R Core Team 2012). Below is the version date information:

**R version 2.15.2** (2012-10-26) -- "Trick or Treat" Copyright (C) 2012 The R Foundation for Statistical Computing ISBN 3-900051-07-0 Platform: x86\_64-w64-mingw32/x64 (64-bit)

R was downloaded from the Comprehensive R Archive Network (CRAN) <u>website</u>. The extension package "Non-detects And Data Analysis (NADA) for environmental data (Lee, 2012) was also used.

There are several reasons R was selected for computational and statistical analysis. Primarily, R can readily import, sort, and compute data from Excel and produce high quality graphical tools for data analysis. Secondly, R extension packages have been developed to accurately handle large amounts of "censored" (non-detect) data at multiple reporting limits. Finally, computations are easily performed on large and small data sets, once the scripts (programming language used to command R to perform analysis) are developed. Adding data to the database will not require rebuilding the R programming language.

### Handling Non-Detects

Data sets with non-detect results, particularly with multiple reporting limits, present complications for data analysis. The Phase I permittees and Ecology formed a non-detect workgroup in 2010 to review statistical approaches for incorporating non-detect data and produced a draft standard operating procedure (SOP) for handling non-detect data (Ecology, 2011). The draft SOP included a literature review of techniques for handling non-detect data. The review covered simple substitution methods with zero, one-half the detection limit, or some other fraction of the detection limit (Ecology, 1993; EPA, 2006, 2009). The review also covered statistical modeling, ranking, or probability techniques depending upon the data distribution, percentage of censored data, and multiple reporting limits (Antweiler and Taylor, 2008; Clarke, 1998; Cohen, 1959, 1976; Ecology, 1992; EPA, 2006, 2009; Helsel, 2005, 2012; Helsel and Cohn, 1988; Hirsch and Stedinger, 1987; Newman et al., 1990; Singh et al., 2002, 2006).

The draft SOP acknowledged the complexity that accompanies data handling when non-detects make up a large fraction of the data set. Though not finalized, the draft SOP laid out a flow chart for decision making for different conditions such as limited sample size. It stopped short of making any recommendations for any specific situation, since the goal was to apply the SOP to many projects and data summaries for the permittees' annual reports.

Since the draft SOP workgroup last met, Dr. Dennis Helsel, a leader in publications on handling censored data, published a new book on the topic. For this interim assessment report, non-detects are handled following his recommendations in "*Statistics for Censored Environmental Data Using Minitab*® *and R*" (Helsel, 2012), which largely agree with the flow chart initiated by the Phase I SOP workgroup.

For this analysis, no substitutions were made for non-detect data, yet the data (ranks) were considered. In combining multiple data sets from the permittees, sample sizes increased and statistical power increased with more observations. This is particularly useful for drawing conclusions at a regional scale. The statistical approaches used to include the non-detect data are described in the following sections.

### **Descriptive Statistical Plots**

Six types of plots, listed below, represent the process used to analyze each parameter individually.

- Jitter Plot
- Probability Plot
- Non-Detects
- Empirical Distribution Function (edf)
- Box Plot by Land Use
- Box Plot by Season

Appendix C contains a description of how to read each of these 6 plots. Appendix D contains a page with all six plots, devoted to each parameter and matrix combination. The pages of plots in Appendix D are also called the "data sheets" in this report.

### **Statistical Calculations**

### Data Distribution

Parameters with better than a 90% rate of detected concentrations were tested using the distribution hypothesis Shapiro-Wilk Test. The Shapiro-Wilk test statistic W tests the null hypothesis that the data came from a normal (or log-normal) distributed population. When the p-value is less than the alpha level of 0.05 (in this study), the null hypothesis is rejected.

Parameters with less than 90% detection rates were not tested using the Shapiro-Wilk test because the test excludes non-detect values and is therefore not reliable for such situations. Alternative methods for testing distribution assumptions to properly include non-detect values may be pursued in the final report.

Probability plots were prepared to assess log-normality of most parameters, including those with less than 90% detection rates. These are visual means to estimate the data distribution for any given parameter. Probability plots are described in Appendix C and shown in Appendix D.

### **Summary Statistics**

Kaplan-Meier (KM) non-parametric statistics were employed to calculate summary statistics (mean, median, standard error, and lower and upper confidence levels). Summary statistics were produced only for parameters whose data sets contained a minimum of a 50% detection rate, categorized as Case A in this report.

Parameters were categorized as Case B if the data set contained greater than a 50% rate of nondetects, or Case C for data sets with greater than 80% non-detects. Due to the interim nature of this report, summary statistics were not produced for Case B or C parameters. The ranges of both detected concentration and reporting limits for non-detected concentrations are reported for Case B and C parameters.

### Land Use Statistic

The edf plot is a simple and effective statistic that effectively compares the distribution of the range of data by land use. It is employed here as an indicator of a land use effect on the stormwater concentrations. The Peto-Prentice score test was used to determine if there were significant differences between the edf curves across four different land uses. Peto-Prentice is a nonparametric test for handling multiple reporting limits without substitution of any kind.

Helsel (2012) reports that the Peto-Prentice version of the generalized Wilcoxon score test has the best overall performance, given data of unequal sample sizes and unequal censoring between groups. The Peto-Prentice test identifies when at least one land use among the four has significantly different concentrations. In R the Peto-Prentice statistic is computed using the "cendiff" command. p Values are not adjusted. Results are shown in Appendix E. Parameters are highlighted in purple shading to indicate parameters with land use significance (Peto-Prentice p-value <0.05); see *Results* section.

For this interim assessment report, each individual land use was not tested for significant differences between the land uses. Summary tables of values (e.g., mean, median) by land use are postponed until the final report when all the data is available. This decision was made to limit premature conclusions and premature management actions based on this interim assessment report. The statistical plots in Appendix D give indications of which land use have the lowest and highest ranges of detected concentrations, and the edf curves and box plots results are summarized in the *Results* section of this report.

## Results

## **Database Representation**

This interim data set comprises 22,049 records in an Excel spreadsheet. A record is an individual row in Excel that represents a value for a parameter. Tables 6 through 8 summarize this database by permittee, period of record, land use, and data type.

<b>Permittee</b> <sup>(a)</sup>		Number of Records			
(years represented)	Land Use Type	2009	2010	2011	2012
	Commercial	134	480	649	
(3)	High-Density Residential	286	517	405	
(3)	Industrial	132	356	417	
	Commercial	309	841	617	402
City of Tacoma	High-Density Residential	338	603	558	374
(4)	Industrial	273	548	505	402
	Commercial		513	838	239
Clark County	High-Density Residential		324	804	390
(3)	Low-Density Residential		400	436	393
Port of Seattle (1)	Commercial	421			
	Commercial	372	947	765	512
Snohomish County	High-Density Residential	540	807	688	496
(+)	Low-Density Residential	498	914	1211	394

Table 6. Number of records for this interim analysis by permittee, land use, and year.

-- Data type is not represented in the database to date or in this interim report.

(a) This interim assessment does not include data from Port of Tacoma, King County, or Pierce County. Their data are anticipated to be included in the final report.

For this report, *Commercial* land use is represented by five permittees. Note that two of these monitoring sites represent primarily parking lot runoff. *Industrial* and *Low-Density Residential* are each represented by only two of the permittees. Data from four permittees comprise the *High-Density Residential* land use.

### Completeness

#### Sediment Data

The stormwater-entrained sediment samples were only collected annually. Therefore, the data are limited to only a few permittees (at most 15 samples) and analyses and discussion are minimal. The final report will evaluate sediment samples to a greater extent.

### Stormwater Data

Ecology used two approaches to estimate the completeness of the data set summarized in this project. The first approach was to count the number of years of monitoring represented by the permittee. Table 7 lists the years and types of data represented by these interim findings. The second method was to count the number of storms, using the date associated with the sampling data.

The number of permittee-years represented (15) out of the total permittee-years (24) (three years for eight permittees) yields approximately 62% completion. This estimate is probably biased high because not all of the data types are represented for each permittee, particularly flow and sediment data.

The number of storms represented in this study was estimated by counting the unique number of dates in the database (Table 8). This is not the same as the number of samples. Both the counties and cities sampled multiple sites per storm date.

The number of storms (283) is an estimate, and if compared to the theoretical 660 mentioned earlier, represents only 43% of storms possible. This is lower than the estimate based on monitoring years (62%). Because these numbers do not agree, Ecology estimates that these interim findings are based on 43-62%, roughly one-half the total amount of data that will make up the final report.

<b>Permittee</b> <sup>(a)</sup>	Data Type	2009	2010	2011	2012
	Stormwater Composites	Yes	Yes	Yes	
City of Seattle	Stormwater Sediment	Yes	Yes	Yes	
	Rainfall and flow				
	Stormwater Composites	Yes	Yes	Yes	Yes
City of Tacoma	Stormwater Sediment				
	Rainfall and flow	Yes	Yes	Yes	Yes
	Stormwater Composites		Yes	Yes	Yes
Clark County	Stormwater Sediment				
	Rainfall and flow				
	Stormwater Composites	Yes			
Port of Seattle	Stormwater Sediment				
	Rainfall and flow				
	Stormwater Composites	Yes	Yes	Yes	Yes
Snohomish County	Stormwater Sediment	Yes	Yes	Yes	Yes
	Rainfall and flow	Yes	Yes	Yes	Yes

 Table 7. Data types and year included in the interim analysis.

-- Data type is not represented in the database to date or in this interim report.

(a) This interim assessment does not include data from Port of Tacoma, King County, or Pierce County. Their data are anticipated to be included in the final report.

	<b>Count of Unique Dates</b>		
	Water	Sediment	
Permittee	Samples	Samples	
City of Tacoma	72	None	
Clark County	65	None	
Port of Seattle	6	1	
City of Seattle	56	2	
Snohomish County	84	5	
Total	283 <sup>(a)</sup>	8	

### Table 8. Estimated number of storms by sample type.

(a)Water dates include both composite and grab sampling dates.

### **Summary Statistics**

#### **Data Distribution**

Table 9 lists the Shapiro-Wilk test results for this study, including the W statistic and p-value. Based on these results, the parameters are divided into three categories: normal, log-normal, and non-parametric. The Shapiro-Wilk tests were run in R on both un-transformed and logtransformed data, using the "shapiro.test" command on only detected concentrations for parameters with a minimum of 10 detections.

These results largely agree with the National Urban Runoff Program (NURP) results. NURP, a large national stormwater study, found that stormwater event mean concentrations (EMCs) for most parameters followed either log-normal distributions or were distribution-free (EPA, 1983).

No other parameters were tested for their adherence to a modeled distribution due to the larger frequencies of non-detects and the interim nature of this report. Although we restricted distribution testing to the parameters with the highest rates of detection, we found that many of the parameter's probability plots (Appendix D) looked nearly linear, indicating log-normal distribution. These will be examined on a case-by-case basis for the final report following Helsel's recommendations.

Parametric			Non-Parametric
Normal	W statistic	p Value	Unknown Distribution
Sediment			Sediment
Total Solids (%)	0.95	0.43	Total organic carbon (%)
Log-Normal Parameters	W statistic	p Value	Benz[a]anthracene (ug/Kg, dw)
Sediment			Benzo(g,h,i)perylene (ug/Kg, dw)
Bis(2-ethylhexyl) phthalate (ug/Kg, dw)	0.94	0.48	Water
Copper (mg/Kg, dw)	0.92	0.19	Conductivity (uS/cm)
Pyrene (ug/Kg, dw)	0.94	0.38	Hardness as CaCO <sub>3</sub> (mg/L)
Zinc (mg/Kg, dw)	0.91	0.12	pH
Chrysene (ug/Kg, dw) <sup>(a)</sup>	0.91	0.17	Chloride (mg/L)
Fluoranthene (ug/Kg, dw) <sup>(a)</sup>	0.93	0.32	Total Suspended Solids (mg/L)
Indeno(1,2,3-cd)pyrene (ug/Kg, dw) <sup>(a)</sup>	0.93	0.27	Nitrite-Nitrate, dissolved (mg/L)
Lead $(mg/Kg, dw)^{(a)}$	0.89	0.1	Total Kjeldahl Nitrogen (mg/L)
Water			Total Phosphorus (mg/L)
Copper (ug/L)	0.99	0.5	Fecal coliform (cfu/100 mL)
Precipitation (in)	0.99	0.08	Magnesium (ug/L)
Turbidity (NTU)	0.99	0.07	Copper, dissolved (mg/L)
Total Phosphorus water (mg/L)	0.99	0.08	Lead (mg/L)
Ortho-phosphate, dissolved (mg/L) <sup>(b)</sup>	0.99	0.17	Zinc (mg/L)
TPH-Dx (subfraction=Heavy Oil Range			
Hydrocarbons) (ug/L) <sup>(b)</sup>	0.99	0.73	Zinc, dissolved (mg/L)

 Table 9. Distribution results for parameters with detection rates >95%.

(a) 14 of 15 samples had "detect" results (>93%)

(b) 105 of 116 samples had "detect" results (>90%)

### **Categorical Evaluations**

A Kaplan-Meier statistical test (non-parametric) was the default choice for calculating summary statistics due to the non-detect data, based on recommendations in Helsel (2012). A non-parametric approach does not impart bias when calculating the summary statistics on data sets with non-detected results. These recommendations are reproduced and discussed below.

This section describes how Ecology summarized the event based stormwater outfall data by parameter. The pragmatic approach used to select statistical tests for summarizing the data for this interim assessment is based on Table 6.11 of Helsel's 2012 book. Helsel recommends use of KM non-parametric statistics when non-detects make up less than 50% of the data set, regardless of the number of observations. This is defined as Case A for these interim findings. Table 10 shows this study's categories called "Case" A, B, or C, and the methods for estimation of summary statistics, based on the percent of the data that was non-detect (censored). Summary statistics (e.g., mean, median, standard error) for each parameter are calculated, where possible. These categorical summary statistics combine all data across the land uses for each given parameter. Summary data were not corrected for significant digits in this interim assessment.

	Amount of Data by Parameter									
Case	Percent Censored	< 50 Observations	> 50 Observations							
А	< 50 % non-detects	Kaplan-Meier	Kaplan-Meier							
B <sup>(a, b)</sup>	50-80 % non-detects	Kaplan-Meier Robust MLE, robust ROS	Kaplan-Meier MLE							
С	> 80% non-detects	Report only % above a meaningful threshold	May report high sample percentiles							

Table 10. Methods for estimating summary statistics.

(a) These interim findings did not differentiate between Case B and Case C and reported only the range of detections and range of non-detections. In the final report, Ecology intends to follow Helsel's recommendation for Case B conditions to estimate summary statistics.

(b) In the final report Ecology intends to follow Helsel's recommendations and use MLE or ROS for Case B, per Table 6.11 of his book for parametric distributions and KM for the non-parametric parameters.

### Case A

Parameters where non-detects make up less than 50% of the data set (Case A) are summarized using KM statistics in Tables 11-13. The NADA for R function "cenfit" command computes the nonparametric KM summary statistics. These statistics are run on all the data for each parameter (not each individual land use). Non-parametric statistics make no assumption about the data's distribution and can also be used on log-normal data sets to develop summary statistics. Summary statistics by parameter and land use will be postponed until the final report when all the data is available. Case A parameters with shading highlights (in Tables 11-13) showed significant differences between land uses (see Appendix E for statistical results). Summary statistics for all parameters by land use will be tabulated in the final report. In cases with few to zero non-detect values, the KM statistics return the correct values for mean and median.

### Case B

Parameters with 50-80% of the data set as non-detects were handled according to the result of the distribution test. For the parameters that follow parametric distributions, Helsel recommends that either imputation methods, robust Maximum Likelihood Estimations (MLE) or robust Regression on Order Statistics (ROS), are followed. However, the majority of the Phase I monitoring parameters that fall into the Case B situation were not found to be parametric.

Since the credibility of summary statistics for the Case B parameters would be low, we felt the best approach for this interim assessment was to report the ranges of detected and non-detected for each Case B parameter. For some of the Case B parameters, a substantial number of samples (greater than 300 in some cases) were collected. For Case B parameters with a high sample number, the probability plot (Appendix D), displays the results. Ranges for Case B parameters are shown in Table 14-17.

Ecology cautions the reader to be mindful, particularly for parameters with a moderate to high frequency of non-detects, that results may change in the final report.

### Case C

Ranges for Case C parameters are also shown in Tables 14 through 17. Typically, Case C parameters have few detected values. According to Helsel's guidance, comparing the range of data is the only valid statistical approach.

Table 18 lists the parameters that were not found in any samples in the interim database (100% non-detect) and those rarely detected (>90% non-detect). Table 18 is sorted by percent non-detect and the parameter group.

				Kaplan Meier (KM) Summary Statistics				
Parameter, Matrix	Case	No. of Samples	% Censored	Mean	Mean Std. Error	Mean 95 LCL	Mean 95 UCL	Median
Conventionals								
Fecal Coliform, water (cfu/100 mL)	А	275	9.1	2783	660	1490	4077	400
Conductivity, water (uS/cm)	А	373	0	129.7	15.6	99.1	160.2	85.0
Hardness as CaCO <sub>3</sub> , water (mg/L)	А	373	0	39.5	4.1	31.4	47.6	29.0
Turbidity, water (NTU)	А	284	0	27.2	1.8	23.6	30.8	18.0
Total Suspended Solids, water (mg/L)	А	347	0.3	57.4	4.1	49.3	65.4	34.7
pH, water (pH)	А	166	0	6.9	0.0	6.9	7.0	7.0
Chloride, water (mg/L)	А	325	3.4	8.7	1.4	5.9	11.4	3.5
Surfactants, water (mg/L)	А	346	43.6	0.06	0.004	0.05	0.07	0.038
Biochemical Oxygen Demand, water (mg/L)	А	303	27.1	7.1	1.5	4.2	10.0	3.6
Total Solids, sediment (%)	А	18	0	35.7	5.0	25.9	45.4	39.5
Total Organic Carbon, sediment (%)	А	15	0	16.2	4.0	8.5	24.0	11.0
Nutrients								
Ortho-phosphate, water dissolved (mg/L)	А	300	10.7	0.033	0.002	0.029	0.037	0.022
Nitrite-Nitrate, water dissolved (mg/L)	А	337	0.6	0.6	0.0	0.5	0.7	0.3
Total Kjeldahl Nitrogen, water (mg/L)	А	328	6.1	1.3	0.1	1.1	1.5	0.9
Total Phosphorus, water (mg/L)	А	332	1.2	0.2	0.0	0.1	0.2	0.1

#### Table 11. Summary statistics for Case A: conventional and nutrient parameters.

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section and Appendix E.

LCL: Lower confidence level

UCL: Upper confidence level
				Kaplan Meier (KM) Summary Statistics			cs	
Parameter	Case	No. of Samples	% Censored	Mean	Mean Std. Error	Mean 95 LCL	Mean 95 UCL	Median
Metals								
Cadmium, sediment (mg/Kg, dw)	А	15	13.3	0.8	0.2	0.4	1.2	0.7
Cadmium, water (ug/L)	А	379	28	0.18	0.02	0.15	0.21	0.11
Cadmium, water dissolved (ug/L)	А	375	40.8	0.1	0.0	0.1	0.1	0.0
Copper, sediment (mg/Kg, dw)	А	15	0	73.1	25.4	23.4	122.9	16.6
Copper, water (ug/L)	А	374	1.3	16.2	0.9	14.4	18.0	10.2
Copper, water dissolved (ug/L)	А	343	2.3	6.1	0.4	5.3	6.9	4.0
Lead, sediment (mg/Kg, dw)	А	15	13.3	74.8	28.9	18.1	131.5	5.9
Lead, water (ug/L)	А	374	1.9	14.5	1.3	12.0	16.9	4.6
Lead, water dissolved (ug/L)	А	364	20.9	1.1	0.2	0.8	1.4	0.2
Magnesium, water (ug/L)	А	179	0	2822	563	1718	3925	1600
Mercury, sediment (mg/Kg, dw)	А	8	12.5	0.1	0.0	0.1	0.2	0.1
Zinc, sediment (mg/Kg, dw)	А	15	0	318	90	142	493	146
Zinc, water (ug/L)	А	370	1.1	107.8	7.3	93.4	122.1	71.7
Zinc, water dissolved (ug/L)	А	356	1.7	58.9	6.0	47.2	70.7	29.8
Total Petroleum Hydrocarbon								
Diesel Range Hydrocarbons, water (ug/L)	А	307	26.7	428	35	360	497	220
Heavy Oil Range Hydrocarbons, water (ug/L)	А	116	9.5	710	115	483	936	270
Heavy Fuel Oil, water (ug/L)	А	119	14.3	915	112	696	1135	480
Lube Oil, water (ug/L)	А	27	14.8	1863	249	1376	2351	1400
Motor Oil, water (ug/L)	А	44	13.6	1334	144	1052	1616	1000

#### Table 12. Summary statistics for Case A: metals and TPHs.

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section and Appendix E.

LCL: Lower confidence level

UCL: Upper confidence level

				Kaplan Meier (KM) Summary Statistics				s
		No. of	%		Mean Std.	Mean 95	Mean 95	
Parameter	Case	Samples	Censored	Mean	Error	LCL	UCL	Median
PAHs								
Anthracene, sediment (ug/Kg, dw)	А	15	33.3	433	271	neg	965	94
Benz[a]anthracene, sediment (ug/Kg, dw)	А	7	0	3829	3363	neg	10420	580
Benzo(a)pyrene, sediment (ug/Kg, dw)	А	15	26.7	2576	2204	neg	6896	220
Benzo(b)fluoranthene, sediment (ug/Kg, dw)	А	12	25	3990	2943	neg	9758	240
Benzo(g,h,i)perylene, sediment (ug/Kg, dw)	А	7	0	4184	3638	neg	11314	540
Benzo(k)fluoranthene, sediment (ug/Kg, dw)	А	12	33.3	3409	2692	neg	8685	198
Chrysene, sediment (ug/Kg, dw)	А	15	6.7	3333	2490	neg	8214	809
Dibenz[a,h]anthracene, sediment (ug/Kg, dw)	А	15	33.3	754	608	neg	1946	79
Fluoranthene, sediment (ug/Kg, dw)	А	15	6.7	6538	4615	neg	15583	1460
Fluoranthene, water (ug/L)	А	369	41.7	0.3	0.11	0.08	0.5	0.03
Indeno(1,2,3-cd)pyrene, sediment (ug/Kg, dw)	А	15	6.7	2852	1594	neg	5975	400
Phenanthrene, sediment (ug/Kg, dw)	А	15	13.3	2646	1917	neg	6404	455
Pyrene, sediment (ug/Kg, dw)	А	15	0	6232	4149	neg	14364	1300
Pyrene, water (ug/L)	А	369	37.1	0.3	0.1	0.1	0.5	0.0
Other Organics								
Bis(2-ethylhexyl) phthalate, sediment (ug/Kg, dw)	А	13	0	6164	1600	3029	9299	4400
Bis(2-ethylhexyl) phthalate, water (ug/L)	А	368	31.2	1.7	0.1	1.5	2.0	0.9
Butyl benzyl phthalate, sediment (ug/Kg, dw)	А	15	46.7	931	524	neg	1958	96
Phenol, sediment (ug/Kg, dw)	А	10	40	206	69	70	341	160
PCB-Aroclor 1254, sediment (ug/Kg, dw)	А	8	37.5	86.6	24.4	38.8	134.5	41.0
p-Cresol, sediment (ug/Kg, dw)	А	7	14.3	1415	968	neg	3312	170

Table 13. Summary statistics for Case A: PAHs and other organic contaminants.

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section and Appendix E.

neg: a low value less than zero.

LCL: Lower confidence level

UCL: Upper confidence level

				Range of Detections		Range on Non-Detects	
		No. of	%	Min Value	Max Value	Min Value of	Max Value of
Parameter, Matrix	Case	Samples	Censored	of Detected	of Detected	Non-Detect	Non-Detects
PAHs							
2-Methylnaphthalene, sediment (ug/Kg, dw)	В	15	60	22.7	110	0.1	52
2-Methylnaphthalene, water (ug/L)	В	371	76.8	0.003	2.5	0.003	2.1
Acenaphthene, sediment (ug/Kg, dw)	В	15	60	12.2	930	0.1	59
Benz[a]anthracene, water (ug/L)	В	246	61	0.004	11	0.002	1
Benzo(a)pyrene, water (ug/L)	В	366	77.3	0.004	15	0.004	1.5
Benzo(b)fluoranthene, water (ug/L)	В	219	69.4	0.02	13	0.017	1.5
Benzo(g,h,i)perylene, water (ug/L)	В	369	58.5	0.003	12	0.003	1
Benzo(k)fluoranthene, water (ug/L)	В	219	79.9	0.049	13	0.024	1.5
Chrysene, water (ug/L)	В	369	56.9	0.003	16	0.003	1
Dibenzofuran, sediment (ug/Kg, dw)	В	7	71.4	56	1100	29	59
Fluorene, sediment (ug/Kg, dw)	В	14	57.1	40.3	1400	0.1	34
Indeno(1,2,3-cd)pyrene, water (ug/L)	В	370	71.4	0.003	10	0.003	1.5
Naphthalene, water (ug/L)	В	367	57.8	0.005	2.2	0.004	2.1
Phenanthrene, water (ug/L)	В	370	51.4	0.006	15	0.003	1
1-Methylnaphthalene, sediment (ug/Kg, dw)	С	13	84.6	11	58	0.1	59
1-Methylnaphthalene, water (ug/L)	С	124	92.7	0.1	1.6	0.1	0.5
Acenaphthene, water (ug/L)	С	370	85.7	0.003	0.61	0.003	2.1
Acenaphthylene, sediment (ug/Kg, dw)	С	15	93.3	210	210	0.1	59
Acenaphthylene, water (ug/L)	С	371	89.8	0.003	0.19	0.003	2.1
Anthracene, water (ug/L)	С	371	90.3	0.004	1.6	0.004	2.1
Dibenz[a,h]anthracene, water (ug/L)	С	369	89.7	0.003	5.3	0.003	2.1
Dibenzofuran, water (ug/L)	С	135	94.8	0.11	0.5	0.018	2.1
Fluorene, water (ug/L)	С	371	83.8	0.003	0.85	0.003	2.1
Naphthalene, sediment (ug/Kg, dw)	С	15	86.7	23.5	410	0.1	59

Table 14. Data and non-detect ranges for PAHs with large percentages of censoring (Case B and C).

				<b>Range of Detections</b>		<b>Range on Non-Detects</b>	
		No. of	%	Min Value	Max Value	Min Value of	Max Value
Parameter, Matrix	Case	Samples	Censored	of Detected	of Detected	Non-Detect	of Non-Detects
Metals							
Mercury, water (ug/L)	С	231	82.7	0.02	2100	0.02	0.2
Mercury, water dissolved (ug/L)	С	231	96.5	0.02	0.4	0.02	0.2
Herbicide							
2,4-D, sediment (ug/Kg)	В	5	80	340	340	50	50
2,4-D, water (ug/L)	В	345	75.9	0.02	28.4	0.05	1.2
Triclopyr, sediment (ug/Kg, dw)	В	5	80	310	310	50	50
Triclopyr, water (ug/L)	С	335	83	0.02	18.3	0.05	1.2
Mecoprop, sediment (ug/Kg, dw)	В	5	80	6500	6500	5000	5000
Mecoprop, water (ug/L)	С	348	83.9	0.02	28	0.02	250
Insecticide							
Chlorpyrifos, sediment (ug/Kg, dw)	С	14	100	NA	NA	0.1	710
Chlorpyrifos, water (ug/L)	С	369	99.2	0.022	0.754	0.006	1
Diazinon, sediment (ug/Kg, dw)	С	14	100	NA	NA	0.1	620
Diazinon, water (ug/L)	С	369	98.1	0.014	0.53	0.005	1
Dichlobenil, water (ug/L)	В	359	59.9	0.012	1.3	0.007	1
Dichlobenil, sediment (ug/Kg, dw)	С	8	87.5	20.5	20.5	0.1	1
Malathion, sediment (ug/Kg, dw)	С	14	100	NA	NA	0.1	360
Malathion, water (ug/L)	С	369	97.8	0.027	0.2	0.008	1
Prometon, sediment (ug/Kg, dw)	С	8	100	NA	NA	0.1	0.5
Prometon, water (ug/L)	С	359	95.3	0.025	3.21	0.005	0.5
Fungicide							
Pentachlorophenol, water (ug/L)	В	344	77.6	0.02	1.2	0.02	2.5
Pentachlorophenol, sediment (ug/Kg, dw)	С	19	84.2	13.5	84.4	1	2200

Table 15. Data and non-detect ranges for metals and pesticides with large percentages of censored data (Case B and C).

NA: not applicable because there were not detected values.

				Range of Detections		Range on Non-Detects	
Parameter, Matrix	Case	No. of Samples	% Censored	Min Value of Detected	Max Value of Detected	Min Value of Non-Detect	Max Value of Non-Detects
Phthalates							
Butyl benzyl phthalate, water (ug/L)	В	369	71.5	0.022	2.82	0.018	2.1
Diethyl phthalate, water (ug/L)	В	371	66.8	0.03	3.7	0.1	1
Di-n-octyl phthalate, sediment (ug/Kg, dw)	В	15	73.3	116	9400	1	440
Dibutyl phthalate, sediment (ug/Kg, dw)	В	15	73.3	98.3	2070	1	440
Dibutyl phthalate, water (ug/L)	В	369	60.2	0.028	5.08	0.023	1
Diethyl phthalate, sediment (ug/Kg, dw)	С	15	100	NA	NA	1	440
Dimethyl phthalate, sediment (ug/Kg, dw)	С	15	93.3	370	370	1	180
Dimethyl phthalate, water (ug/L)	С	371	80.9	0.027	2.8	0.021	2.1
Di-n-octyl phthalate, water (ug/L)	С	367	88.3	0.018	2.2	0.018	2.1
BTEX and TPH-Gx							
Benzene, water (ug/L)	С	120	99.2	2.6	2.6	1	1
Ethylbenzene, water (ug/L)	С	120	100	NA	NA	1	1
Toluene, water (ug/L)	С	120	97.5	1.1	2.07	1	1
Total xylenes, water (ug/L)	С	120	99.2	1.73	1.73	1	1
Gasoline Range Hydrocarbons, water (ug/L)	С	317	81.7	10.6	395	10	250

Table 16. Data and non-detect ranges for phthalates and hydrocarbons with large percentages of censored data (Case B and C).

NA: not applicable because there were not detected values.

				<b>Range of Detections</b>		Range on Non-Detects	
		No. of	%	Min Value	Max Value	Min Value of	Max Value of
Parameter	Case	Samples	Censored	of Detected	of Detected	Non-Detect	Non-Detects
Phenols (sediment only)							
2,4,5-Trichlorophenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
2,4,6-Trichlorophenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
2,4-Dichlorophenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
2,4-Dimethylphenol (ug/Kg, dw)	С	7	85.7	10.9	10.9	10	440
2,4-Dinitrophenol (ug/Kg, dw)	С	7	100	NA	NA	10	4400
2-Chlorophenol (ug/Kg, dw)	С	7	100	NA	NA	10	440
2-Nitrophenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
4,6-Dinitro-2-Methylphenol (ug/Kg, dw)	С	7	100	NA	NA	10	4400
4-Chloro-3-Methylphenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
4-Nitrophenol (ug/Kg, dw)	С	7	100	NA	NA	10	2200
o-Cresol (ug/Kg, dw)	В	7	71.4	14.1	39.3	10	440
PCBs (sediment only)							
PCB-aroclor 1260 (ug/Kg, dw)	В	8	62.5	80	100	0.05	48
PCB-aroclor 1016 (ug/Kg, dw)	С	8	100	NA	NA	0.05	54
PCB-aroclor 1221 (ug/Kg, dw)	С	8	100	NA	NA	0.05	54
PCB-aroclor 1232 (ug/Kg, dw)	С	8	100	NA	NA	0.05	54
PCB-aroclor 1242 (ug/Kg, dw)	C	8	100	NA	NA	0.05	54
PCB-aroclor 1248 (ug/Kg, dw)	C	8	87.5	45	45	0.05	54

Table 17. Data and non-detect ranges for phenols and PCBs with large percentages of censored data (Case B and C).

NA: not applicable because there were not detected values.

Table 18.	Parameters	with high	frequency	of non-detection.
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Poromotor Matrix	Casa	% Consorad	# of Somplos	Analytical Mathod	Parameter
Completely non-detect (100% censored)	Case	Cellsoreu	Samples	Methou	Group
Ethylbenzene water (ug/I)	C	100	120	FPA 624	BTFX
PCB-aroclor 1016 sediment (ug/Kg dw)	C	100	8	EPA 8082	PCBs
PCB-aroclor 1221 sediment (ug/Kg, dw)	C	100	8	EFA 8083	PCBs
PCB-aroclor 1221, sediment (ug/Kg, dw)	C	100	8	EPA 8084	PCBs
PCB-aroclor 1242 sediment (ug/Kg, dw)	C C	100	8	EPA 8085	PCBs
2.4.5-Trichlorophenol sediment (ug/Kg dw)	C	100	8 7	EPA 8270D	BNAs
2.4.6-Trichlorophenol, sediment (ug/Kg, dw)	C	100	, 7	EPA 8270D	BNAs
2.4-Dichlorophenol sediment (ug/Kg dw)	C	100	, 7	EPA 8270D	BNAs
2,4-Dinitrophenol, sediment (ug/Kg, dw)	C	100	, 7	EPA 8270D	BNAs
2-Chlorophenol sediment (ug/Kg dw)	C	100	, 7	EPA 8270D	BNAs
2-Nitrophenol, sediment (ug/Kg, dw)	C	100	, 7	EPA 8270D	BNAs
4.6-Dinitro-2-Methylphenol, sediment (ug/Kg, dw)	C	100	7	EPA 8270D	BNAs
4-Chloro-3-Methylphenol, sediment (ug/Kg, dw)	C	100	7	EPA 8270D	BNAs
4-Nitrophenol, sediment (ug/Kg, dw)	C	100	7	EPA 8270D	BNAs
Malathion, sediment (ug/Kg, dw)	C	100	14	EPA 8270D	BNAs
Chlorpyrifos, sediment (ug/Kg, dw)	C	100	14	EPA 8270D	Pesticide
Diazinon, sediment (ug/Kg, dw)	C	100	14	EPA 8270D	Pesticide
Diethyl phthalate, sediment (ug/Kg, dw)	С	100	15	EPA 8270D	Phthalate
Prometon, sediment (ug/Kg, dw)	С	100	8	EPA 8270D	Phthalate
Rarely Detected (>90% censored)					
Benzene, water (ug/L)	С	99.2	120	EPA 624	BTEX
Total xylenes, water (ug/L)	С	99.2	120	EPA 624	BTEX
Chlorpyrifos, water (ug/L)	С	99.2	369	EPA 8270D	Pesticide
Diazinon, water (ug/L)	С	98.1	369	EPA 8270D	Pesticide
Malathion, water (ug/L)	С	97.8	369	EPA 8270D	Pesticide
Toluene, water (ug/L)	С	97.5	120	EPA 624	BTEX
				EPA 245.1 or	
Mercury, water dissolved (ug/L)	С	96.5	231	SM 7470A	Metals
Prometon, water (ug/L)	С	95.3	359	EPA 8270D	Pesticide
Dibenzofuran, water (ug/L)	С	94.8	135	EPA 8270D	BNAs
Acenaphthylene, sediment (ug/Kg, dw)	C	93.3	15	EPA 8270D	PAH
Dimethyl phthalate, sediment (ug/Kg, dw)	C	93.3	15	EPA 8270D	Phthalate
1-Methylnaphthalene, water (ug/L)	C	92.7	124	EPA 8270D	PAH
Anthracene, water (ug/L)	C	90.3	371	EPA 8270D	PAH

# Land Use Significance

A simple and effective statistic (Peto-Prentice) effectively compares the distribution of the range of data (the edf plot) by land use and is employed here as an indicator of a land use effect on the stormwater concentrations. Because this interim assessment represents only approximately one-half of the data collected by the Phase I permittees, the reader should consider significant differences in concentrations based on land use to be tentative findings. This is particularly true for the parameters with land use significance based on low sample numbers (e.g., many of the sediment samples), where additional data will likely redefine the relationships.

Based on the available data, some parameters, even with censored values, show significant difference between the four land use groups. Table 19 lists the Case A parameters with interim evidence of statistically different concentrations among the monitored land uses.

Conventionals	Nutrients	Total Petroleum Hydrocarbon
Fecal coliform	Ortho-phosphate as P	Diesel range hydrocarbons
Conductivity	Nitrite-Nitrate as N	Heavy oil range hydrocarbons
Hardness as CaCO <sub>3</sub>	Total Kjeldahl nitrogen	Heavy fuel oil
Turbidity	Total phosphorus	Lube oil water
Total suspended solids		
pH	Metals	PAHs
Chloride	Cadmium (total and dissolved)	Chrysene in sediments
Surfactants	Copper (total and dissolved)	Fluoranthene in water and sediments
Biochemical oxygen demand	Lead (total and dissolved)	Pyrene in water and sediments
	Magnesium water (ug/L)	
	Zinc (total and dissolved)	Other Organics
	Zinc in sediments	Bis(2-ethylhexyl) phthalate

 Table 19. Case A parameters with evidence of differences in concentrations by land use.

Summary tables of values (e.g., mean, median) by land use are postponed until the final report when all the data are available.

# **Comparisons to other stormwater studies**

The median concentrations from this study are compared in the following sections to the median concentrations of a few other stormwater studies where data exist.

- Review of the Nationwide Urban Runoff Program (NURP) (EPA, 1983).
- Nonparametric Statistical Tests Comparing First Flush and Composite Samples from the National Stormwater Quality Database (NSQD) (Maestre et al., 2004).
- The National Stormwater Quality Database, Version 1.1; A Compilation and Analysis of NPDES Stormwater Monitoring Information (Maestre et al., 2005) <u>http://rpitt.eng.ua.edu/Publications/Stormwater%20Characteristics/NSQD%20EPA.pdf</u>
- Control of Toxic Chemicals in Puget Sound: Phase 3 Data and Load Estimates (Herrera, 2011) (called *Toxics in Surface Runoff Study* in this document).

Comparisons made to these other studies are informative for these interim findings and are included to give context to the results of this study.

The NURP study was a research project conducted by the U.S. Environmental Protection Agency (EPA) between 1979 and 1983. NURP was the first comprehensive study of urban stormwater pollution across the United States and established the national stormwater quality benchmark. Samples were collected to represent the event mean concentrations of the runoff event, which allows us to compare results from the permittees directly. The study evaluated the stormwater data distributions and concluded that 90% of their study parameters followed a log-normal distribution.

The NSQD was created in the mid-1980s to store stormwater data collected by the NURP study and other Phase I MS4 data. Over time, the database gained some specialized U.S. Geological Survey stormwater studies and more recently selected outfall data from International BMP Database. Several reports have been published by Alex Maestre and Robert Pitt, summarizing the stormwater monitoring data contained in versions of the database over the last 20 years (Version 1.0, 1.1 and 2). Version 3 of the NSQD is available online at: <a href="http://unix.eng.ua.edu/~rpitt/Research/ms4/mainms4.shtml">http://unix.eng.ua.edu/~rpitt/Research/ms4/mainms4.shtml</a>.

## Non-Detected Data in Stormwater Monitoring Literature

In the NSQD Version 1.1 review, Maestre et al. (2005; Chapter 3) provides a review of how non-detects have been handled in stormwater studies. Most recent environmental and particularly stormwater studies have used substitution techniques to substitute one-half or full value of the method detection limit for the value of the non-detect. This has been a common practice for data sets with relatively few non-detect data points. Antweiler and Taylor (2008) indicate that using substitutions for non-detects produce comparable summary statistics.

In the NURP study, non-detected data were summarized using substitution of the value of the reported detection limit. In the NSQD version 1.1 data summary, non-detected values were estimated using the Cohen's maximum likelihood method (a method that randomly generates the missing data based on the known probability distributions of the data (Maestre et al., 2005).

The *Toxics in Surface Runoff Study* estimated the non-detect values by substituting one-half the value of the detection limit (Herrera, 2011). Comparisons of the permittee's data results to NURP, NSQD, and the *Toxics in Surface Runoff Study* are considered approximate because the methods for sample collection and data analysis differed between all of the studies. Comparisons to the results from the Toxics in Runoff Study are weaker due to the differences in sample collection. The permittees collected flow-weighted composites from direct stormwater discharges across 75% of the storm event, whereas the *Toxics in Surface Runoff samples* were collected as grab samples from the receiving waters during storm events. The instream concentrations as captured by the *Toxics in Surface Runoff Study* were anticipated to be lower than direct stormwater runoff concentrations, particularly in urban areas.

Despite different methods for handling non-detects, comparisons of median values are retained in this report because the NURP and NSQD represent the earliest and largest national stormwater quality characterization efforts in the United States, and the *Toxics in Surface Runoff Study* is the most recent regional publication with wet weather surface water concentrations for toxic pollutants. Fortunately, in the case of the NURP and NSQD, most of the parameters monitored are limited to the conventional, nutrients, and metals where non-detections are infrequent and typically influence summary statistics less.

# **Contaminant Concentrations**

This section summarizes the stormwater and stormwater sediment concentration data. The goal of this section is to discuss the variability and median concentrations and the significance of land use on the concentrations. For this report of interim findings, pair-wise comparisons were not conducted, so the land uses with significant differences are not known. However, indications of the land use effects are discussed in the *Methods* section of this report and shown in the edf plots for each parameter. For all the parameters discussed in this section the data sheets and statistical plots are shown in Appendix D and the results of the land use analysis (Peto-Prentice test) are found in Appendix E.

The range of detected concentrations (lowest and highest) is illustrated in Figures 4-8 for parameter groups. Detected concentrations are records that were not flagged as non-detect "U". This includes results with no flag or records with an associated "J" flag indicating the result is estimated. These graphs are outputs of R. The reader should be aware of the log scale on the x-axis depicted in scientific notation. A reading of 1e+01 is equivalent to a value of 10.

Not every parameter in the database is shown in Figures 4-8 for two reasons. First, a particular parameter may not have any detected concentrations. Parameters with very low detection frequencies are discussed in more detail below. Second, not all parameters are conveniently grouped in these tables (e.g., grain size).

### **Conventional Parameters**

The conventional parameters (Figure 4) were detected with high frequency (except surfactants). All the conventional parameters are considered as Case A for summary statistic calculations. All of the water conventional parameters were also found to have at least one land use where

concentrations are significantly different. The only two conventional parameters without land use effects are the two solids analyses: total solids and total organic carbon.



# Figure 4. Ranges of values for detected conventional parameters in WA Phase I Stormwater 2007-2012.

#### Fecal Coliform

Fecal coliform concentrations ranged more than four orders of magnitude. The stormwater median concentration for the entire data set (n=275) was 400 cfu/100 mL, Table 11. For comparison, the NSQD case study (Maestre et al., 2004) reported median from the combined land uses was 46,238 mpn/100 mL. In this interim assessment, fecal coliform results were reported in both cfu/100 mL and mpn/100 mL (Table 5). The units were assumed to be equivalent and the data results were combined. The Peto-Prentice test indicates that fecal coliform concentrations are significantly different among the four land uses. Based on the edf curve, the low-density residential land use appears to have lower values than the other land uses.

#### Conductivity, Hardness, pH, and Chloride

Concentrations of conductivity, hardness, pH, and chloride are useful indicators for water quality and play a role in determining pollutant source activities.

Conductivity of the stormwater discharges ranged from 7.2 to 5,330 uS/cm, and the median value was 85 uS/cm. Conductivity directly measures electrical conductance and is often related to total dissolved solids content of the water.

The pH of stormwater discharges ranged 5.6 to 8.3. The median and mean concentrations for pH were 7.0 and 6.9, respectively, slightly below the reported median of 7.2 from the NSQD case study (Maestre et al., 2004). The pH of precipitation in western Washington was consistently between 5.0 - 5.3 for 2007-2012 (NOAA website, accessed 2013).

Hardness values in stormwater ranged from 3.4 to 1,300 mg/L. The median was 29 mg/L, which is generally considered "soft" water. Values over 160 mg/L are considered very hard and are a concern for water delivery systems due to the production of scale deposits on the surfaces of pipes or the tendency to induce galvanic corrosion in pipes.

Chloride concentrations in stormwater ranged from 0.003 to 349 mg/L. The median value was 3.53 mg/L.

The Peto-Prentice test tentatively identified stormwater concentrations for these four parameters varied by land use, indicating that at least one land use among the four has significantly different concentrations. For conductivity, hardness and chloride it is not readily apparent which land use(s) would be different from the edf curves or box plots (Appendix D). The Peto-Prentice test and pair-wise type tests will be conducted to further evaluate these tentative findings on the complete data set.

#### Surfactants and Biochemical Oxygen Demand

Surfactants were measured as methylene blue activated substance (MBAS), a colorimetric analysis that uses methylene blue to detect the presence of anionic surfactants (such as a detergent or foaming agent) in water. The median for MBAS was 0.038 mg/L and ranged from 0.017 to 0.665 mg/L.

Biological oxygen demand (BOD) is the measure of oxygen consumed by aerobic biological organisms breaking down organic matter over five-day incubation at 20°C. It is commonly used to estimate organic pollution in water. BOD values ranged from 1.2 to 434 mg/L. The median stormwater value for BOD was 3.6 mg/L, whereas the mean was 7.1 mg/L. BOD results contained 27% non-detects. This finding may be valid and pertain to a particular land use and/or may be an indication of an insensitive laboratory method. The reporting limit specified in the permit was 2.0 mg/L.

The NURP study found stormwater event concentrations varied by land uses for BOD. The reported stormwater event median concentrations for residential areas was 10 mg/L, the commercial land use was 9.3 mg/L, and the mixed land use median was 7.8mg/L (EPA, 1983).

The Peto-Prentice test indicates there is a significant difference among the four land uses for BOD and MBAS parameters. The edf curves show low-density residential far below the concentrations for industrial and commercial in both cases. Land use and seasonal findings will be statistically evaluated in the final report.

### Turbidity and Total Suspended Solids

Turbidity is the degree of light scatter, measured in nephelometric turbidity units (NTU), and indicates either the particulate content or cloudiness of the water. The range for turbidity was from 1 to 200 NTU. The median value for turbidity was 18 NTU, slightly lower than the NSQD case study median for all combined land uses of 21.7 NTU (Maestre et al., 2004).

The Peto-Prentice test indicates there is a significant difference among the four land uses for both turbidity and total suspended solids (TSS) in this interim assessment. The range of values for the industrial land use is narrower than for the other land uses. Because turbidity results

contain no non-detects, the edf curves and box plots show the same information. The final report will evaluate this tentative finding.

TSS is a routine measure of the particulate and solids content. The stormwater event median value for TSS was 34.7 mg/L, the range of detected results was from 1 to 556 mg/L. The NURP stormwater event medians for TSS ranged from 67 to 101 mg/L for mixed and residential land uses, respectively (EPA, 1983). The *Toxics in Surface Runoff Study* receiving water storm-event concentration was 7 mg/L (Herrera, 2011), much lower than the stormwater results from this study and NURP results.

## Nutrients

The nutrient concentrations in stormwater were Case A parameters and summary statistics are presented in Table 11. Figure 5 presents the range for the detected results and the percent detection rate.



% Detected

Figure 5. Ranges of values for detected nutrients in WA Phase I Stormwater 2007-2012.

#### Phosphorus

Ortho-phosphate as P (ortho-phosphate) and total phosphorus were monitored. Concentrations for ortho-phosphate ranged from 0.004 to 0.26 mg/L. The stormwater event median concentration of ortho-phosphate (0.022 mg/L) was an order of magnitude lower than the NSQD case study combined land use median (0.19 mg/L) (Maestre et al., 2004).

The median total phosphorus concentration (0.12 mg/L) was lower than the NSQD case study combined land uses concentration of 0.28 mg/L (Maestre et al., 2004) and the urban land use medians as monitored by the NURP study (0.2 -0.38 mg/L) (EPA, 1983). On the other hand, this study's total phosphorus median of 0.12 mg/L was an order of magnitude higher than the *Toxics in Surface Runoff Study* receiving water storm-event concentration of 0.054 mg/L (Herrera, 2011).

The Peto-Prentice test indicates there is a significant difference among the four land uses for ortho-phosphate and total phosphorus interim results. For ortho-phosphorus, the edf curves show low-density residential land use is well above the other three land uses (industrial, commercial, and high-density residential). There also appears to be a seasonal effect on the stormwater

concentrations, with the summer median exceeding the 75<sup>th</sup> percentile of the winter and spring concentrations. A pair-wise comparison in the final report will be needed to evaluate this tentative finding.

Stormwater concentrations varied less by land use for total phosphorus than ortho-phosphorus, however the Peto-Prentice test does indicate there is a significant difference for one of four land uses. The final report will statistically evaluate this tentative finding.

#### Nitrogen

Nitrite-Nitrate as N (nitrate-nitrite) and total Kjeldahl nitrogen (TKN) were monitored. Concentrations for nitrite-nitrate ranged from 0.024 to 4 mg/L. The median concentration (0.28 mg/L) was lower than nitrite-nitrate median values from the NURP study, which ranged from 0.56 to 0.74 mg/L across land uses (EPA, 1983). The median for the combined land uses was 0.70 mg/L in the NSQD case study (Maestre et al., 2004). The stormwater event median nitrite-nitrate from these interim findings was slightly lower than the *Toxics in Surface Runoff Study* receiving water storm-event median concentration of 0.345 mg/L (Herrera, 2011).

Detected concentrations for TKN ranged from 0.04 to 25 mg/L. The median stormwater TKN concentration (0.93 mg/L) was lower than the NSQD case study combined land uses concentration of 1.5 mg/L (Maestre et al., 2004) and lower than the urban land uses median concentrations (1.18 to 1.90 mg/L) found in the NURP study (EPA, 1983).

The range of observed concentrations overlapped substantially for each land use, for both nitrite-nitrate and TKN concentrations. However, the Peto-Prentice test does indicate there is a significant difference for one of four land uses. There also appears to be a slightly higher summer seasonal high in concentrations for both nitrogen species; however, this has not been tested for significance. The final report will statistically test for land use and seasonal significance.

## Metals

Metals results in water are given in ug/L, also referred to as parts per billion (ppb). For storm sediments, the units are mg/Kg, which is parts per million (ppm). This is fairly typical in surface waters and sediment environmental monitoring studies. Cadmium, copper, lead, and zinc concentrations in water (total and dissolved) are shown in Figure 6. These four metals in water and sediments were treated as Case A parameters and summary statistics are presented in Table 12. Mercury was a Case B parameter and is presented in Table 15. Metals data plots are presented in Appendix D. The storm sediment samples were collected only in the summer season and have very few sample numbers.



Figure 6. Ranges of values for detected metals in WA Phase I Stormwater 2007-2012.

#### Cadmium

Concentrations for dissolved cadmium ranged from 0.003 to 1.85 ug/L, whereas the concentrations for total cadmium ranged from 0.025 to 4.06 ug/L. Non-detect thresholds for dissolved cadmium ranged up to 0.2 ug/L and for total cadmium up to 1 ug/L. The stormwater event median concentration for dissolved cadmium was 0.035 ug/L, and total recoverable cadmium was 0.114 ug/L. The total cadmium median from the NSQD study for all land uses (0.6 ug/L) was higher than that of these findings (Maestre et al., 2004).

Total and dissolved cadmium concentrations were generally interspersed with the non-detect thresholds. The edf plots for both total and dissolved, show that the four land use curves are distinguished. The industrial and commercial area stormwater concentrations show higher

concentrations. The box plot for the industrial area is the only land use to emerge from the uncertainty imposed by the non-detects. The low-density residential stormwater concentrations had the highest percent of non-detections for dissolved (49%) and total (53%). There does not appear to be a seasonal component to stormwater cadmium concentrations.

These results compare well with the *Toxics in Surface Runoff Study*. Both studies found concentrations and detection frequencies for cadmium from commercial/industrial areas were higher than from the other land uses. The medians reported for dissolved (0.03 ug/L) and total (0.05 ug/L) cadmium were lower in the *Toxics in Surface Runoff Study* than in these interim findings (Herrera, 2011).

Stormwater sediment concentrations of cadmium ranged two orders of magnitude (0.02 to 2 mg/Kg).

### Copper

Stormwater concentrations for dissolved copper ranged from 0.31 to 79.4 ug/L, whereas the concentrations for total copper ranged from 0.85 to 151 ug/L. The stormwater event median concentration for dissolved copper was 4 ug/L, and total recoverable copper was 10.2 ug/L. The median total copper result in the NSQD study for all land uses (15 ug/L) (Maestre et al., 2004) was higher than in these findings.

Total and dissolved copper concentrations were frequently detected, with less than 3% of the entire data set as non-detects. The edf plots show the four land use curves are distinguished for both total concentrations and a little less so for the dissolved concentrations. The industrial and commercial area stormwater concentrations are higher than those for the other land uses. This is replicated in the box plots by land use where the industrial and particularly commercial areas have higher total and dissolved concentrations. Low Peto-Prentice p-value scores indicate significance. The dissolved copper Peto-Prentice p-value for significance difference in stormwater concentrations by land use was the second lowest value (2.6E-37) for these interim findings. Conductivity was lowest, at 1.2E-46.

There are three unusually high non-detect thresholds in the dissolved copper results (up to 12.5 ug/L) that appear to cause the "curtain" over the box plots by land use and season. If present in the final data set, these three results will be investigated in the final report. Meanwhile the reader may look past these to see the pattern in the data. There may be a seasonal component to the dissolved copper concentrations.

These results compare well to the *Toxics in Surface Runoff Study* that showed concentrations and detection frequencies for copper from commercial/industrial areas were higher than those from other land uses. The medians reported for dissolved (2.03 ug/L) and total (3.24 ug/L) copper were lower in the *Toxics in Surface Runoff Study* (Herrera, 2011) than in these interim findings.

Stormwater sediment concentrations of copper ranged three orders of magnitude (0.19 to 361 mg/Kg); the median was 73 mg/Kg.

### Lead

Concentrations for dissolved lead ranged from 0.016 to 28 ug/L. Non-detect thresholds reached as high as 1.8 ug/L. Concentrations for total lead ranged from 0.1 to 204 ug/L, and the maximum non-detect was 1 ug/L. The stormwater event median concentrations for dissolved and total lead were 0.175 ug/L and 4.62 ug/L, respectively.

These lead concentrations are higher for the stormwater data than for the *Toxics in Surface Runoff Study* instream storms flows, which were 0.12 ug/L for dissolved lead and 0.50 ug/L for total lead (Herrera, 2011).

The median total lead concentration (4.62 ug/L) was lower than that of the NSQD case study combined land uses concentration of 13 ug/L (Maestre et al., 2004), and lower than the urban land uses median concentrations (104-144 ug/L) found in the NURP study (EPA, 1983).

Lead concentrations (total) were frequently detected with less than 2% of the entire data set as non-detects. Dissolved lead had more non-detects, up to 20% for the entire data set. Only the commercial land use had less than 10% non-detect.

The edf plots show four distinct land use curves for total and dissolved lead concentrations. Stormwater in commercial areas appeared to show higher dissolved and total lead concentrations than the other three land uses. High-density residential and industrial areas appear to have overlapping ranges, particularly at the higher concentrations. Interestingly, the NURP study found that residential areas in the 1980s had the highest median stormwater concentrations. These interim results indicate stormwater concentrations from commercial areas are higher than industrial and residential areas. The Peto-Prentice p-value testing for significance difference in stormwater concentrations by land use was significant (1.2E-21) for dissolved lead and (4.4E-35) for total lead. Statistical analyses to determine whether any significant differences actually exist will be conducted on the entire data set for the final report.

Storm sediment concentrations of lead ranged three orders of magnitude (0.36 to 416 mg/Kg). The median was 5.85 mg/Kg.

#### Mercury

Mercury was found by these interim findings to be a Case B and C parameter. High levels of non-detects were reported: 83% for total mercury and 97% for dissolved mercury. The range of detected concentrations and non-detected thresholds are shown in Table 15. Appendix D data sheets for mercury (total) show one result value of 2,100 ug/L. This result will be investigated in the final report. All other results are below 1 ug/L for total mercury.

#### Zinc

Dissolved zinc concentrations ranged from 0.219 to 1,090 ug/L, four orders of magnitude. Non-detect thresholds reached as high as 36.5 ug/L. Concentrations for total zinc ranged from 4.55 to 1,150 ug/L, and the maximum non-detect concentration was 1 ug/L. Total zinc concentrations were reported with less than 2% of the entire data set as non-detects. The median dissolved zinc concentration (29.8 ug/L) is similar to the median dissolved zinc value (29.1 ug/L) found in the *Toxics in Surface Runoff Study* receiving waters under storm flows (Herrera, 2011). The total zinc median in these interim findings was (71.7 ug/L), nearly double the median in the *Toxics in Surface Runoff Study* (37.2 ug/L total zinc) (Herrera, 2011). However, the median was much lower than the combined land uses concentration of 125.9 ug/L found in the NSQD case study (Maestre et al., 2004) and also lower than the urban land uses median concentrations (135-226 ug/L) found in the NURP study (EPA, 1983).

The Peto-Prentice p-value testing for significance differences in stormwater concentrations by land use was significant for dissolved and total zinc. The data plots (Appendix D) show the concentrations of zinc appear to be lowest in low-density residential areas, and to a lesser extent high-density residential. Stormwater concentrations of dissolved zinc from high-density residential areas better match the range distribution found in the industrial and commercial areas. Concentrations of total zinc are highest from stormwater draining commercial and industrial areas.

Zinc concentrations within the storm sediments were also tentatively found to have land use significance, although this data set is limited at this time. Storm sediment concentrations of zinc ranged from 1.39 to 960 mg/Kg; the median was 146 mg/Kg.

# TPH and BTEX

Stormwater concentrations for the five sub-categories of TPH-Dx (diesel fraction) were all considered Case A parameters, and summary statistics are presented in Table 12. Four of the sub-categories (Diesel Range Hydrocarbons, Heavy Oil Range Hydrocarbons, Heavy Fuel Oil, and Lube Oil) were also found to have a land use difference. Motor oil, the fifth TPH-Dx sub-category, was the only one not found to differ among the land uses; this is likely a ubiquitous pollutant.

As described earlier in the *Methods* section, Ecology developed a summation approach to report on the multiple fractions of hydrocarbons measured by the TPH analytical methods, particularly TPH-Dx. For this interim report, the various categories for TPH-Dx are preserved and reported. Since TPH-Dx results were not summarized as a grand total, a direct comparison to the *Toxics in Surface Runoff Study* is not feasible.

Stormwater concentration data for TPH-Gx (gasoline fraction) was largely non-detected (82%) despite more than 300 samples, a Case C parameter. All of the four BTEX compounds (benzene, toluene, ethylbenzene, xylene) were found to be Case C parameters. The ranges are presented in Table 17. Gasoline and BTEX compounds are volatile organics; therefore, we are not surprised by the results. Detections of volatiles in stormwater would be an indication of a nearby leak, because they volatilize out of the stormwater samples within minutes.

## PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different organic contaminants that form from the incomplete combustion of hydrocarbons, such as coal, oil, gas, garbage, and gasoline (<u>ASTDR website</u> accessed 2013; EPA, 2008). A major source of PAHs in urban stormwater can be from asphalt treatments (Van Metre et al., 1996). PAHs are an environmental concern because they are persistent, toxic to aquatic life, and are suspected human carcinogens.

The list of PAHs monitored included:

- 1-methylnaphthalene
- 2-methylnaphthalene
- acenapthene<sup>1</sup>
- acenaphthylene<sup>1</sup>
- anthracene<sup>1</sup>
- benzo(a)anthracene<sup>1</sup>
- benzo(a)pyrene<sup>1,2</sup>
- benzo(b)fluoanthene<sup>1</sup>
- benzo(k)fluoranthene<sup>1</sup>
- benzo(g,h,i)perylene<sup>1</sup>
- chrysene<sup>1</sup>
- dibenz[a,h]anthracene<sup>1</sup>
- fluoranthene<sup>1</sup>
- fluorene<sup>1</sup>
- indeno(1,2,3-cd)pyrene<sup>1</sup>
- naphthalene<sup>1</sup>
- phenanthrene<sup>1</sup>
- pyrene<sup>1</sup>

<sup>1</sup> On EPA's Priority Pollutant List Appendix A to 40CFR Part 423 (<u>EPA Priority Pollutants website</u>, accessed 2013). <sup>2</sup> On EPA's Persistence, Bioaccumulation and Toxicity (PBT) list (<u>EPA PBT website</u>, accessed 2013).

These PAHs were monitored in both stormwater and storm sediments. Table 13 shows the PAH compounds that were treated as Case A and summary statistics produced. PAHs were detected more frequently in storm sediments than in water, with 12 of the Case A PAHs being from the sediment matrix. This is consistent with the current understanding that PAH compounds are lipophilic and the larger compounds are less soluble in water.

Summing across a categorical type of PAH is common among the literature, but it was not performed in this interim assessment due to the need to evaluate handling of the large numbers of non-detects for summing. This will be a topic for the final report.

Concentrations of many PAHs from the stormwater matrix were largely below detection thresholds. Table 14 lists the Case B and C PAHs. Data plots for each monitored individual PAH are presented in Appendix D. Figure 7 shows the range of PAHs concentrations with detected concentrations. One PAH, 2-methylnaphthalene, is not shown because there were no detected concentrations.

The Peto-Prentice test statistic indicates that several PAHs were found to be significant among the four land uses. Fluoranthene and pyrene were tentatively found to be significant in both water and sediment, among the land uses. Chrysene in sediments was weakly significant between the land uses. These findings are based on only 15 samples and may change with additional data.



Figure 7. Ranges of values for detected PAHs in WA Phase I Stormwater 2007-2012.

## Phthalates

Phthalates are plasticizers used primarily to soften plastics, but they also can be used in a wide variety of commercial products including glues, toys, paints, and pharmaceuticals (Ecology phthalate website, accessed 2013). The following phthalates are on the priority pollutant list (EPA Priority Pollutants website, accessed 2013):

- bis(2-Ethylhexyl) phthalate (BEHP; also known as di(2-Ethylhexyl) phthalate or DEHP)
- Butyl benzyl phthalate (BBP)
- Diethyl phthalate
- Dimethyl phthalate
- di-n-butyl phthalate
- di-n-octyl phthalate

Table 13 presents summary statistics for BEHP and BBP as Case A parameters. Most of the phthalates were found to be Case B and C parameters, and the ranges of detected values are listed in Table 16. Each individual phthalate data sheet is presented in Appendix D. Figure 8 shows the detected-only ranges for phthalates in stormwater.

% Detected



#### Figure 8. Ranges of values for detected phthalates in WA Phase I Stormwater 2007-2012.

BEHP was detected more frequently in stormwater draining commercial areas (12.6% non-detects) than in low-density residential areas (70.6% non-detects). The median BEHP concentration in stormwater was 2.4 ug/L, substantially higher than the median concentration of 0.34 ug/L found from commercial/industrial subbasins in the *Toxics in Surface Runoff Study* (Herrera, 2011). The median BEHP concentration was 4,400 ug/Kg in storm sediments.

The Peto-Prentice p-value testing for significance difference in stormwater concentrations by land use was significant for BEHP in stormwater. The data sheet plots show that the concentrations appear to be lowest in low-density residential areas. Stormwater concentrations of BEHP were equivalent among the other land uses.

## Pesticides

Phase I permittees monitored for pesticides listed in Table 3, in both water and storm sediment, but the required lists for each sample fraction were different. Stormwater concentrations for all of the pesticides were largely below detection limits. Non-detect data comprised over 80% for pesticides, with the sole exception of dichlobenil at 60%. These parameters were categorized into Case B or C (Table 15), despite more than 300 samples in this database.

Because there is such a large data set, the probability plot (Appendix D) for each Case B parameter is still valuable. The probability plot takes into account the rank position of the non-detects and accurately depicts data percentile distribution. The Case B pesticides in water are 2,4-D, Dichlobenil, and pentachlorophenol. As stated earlier, in the case of dichlobenil the median value can be visually estimated as below the last detected value (black dots) and crosses the log-normal distribution line just above the 0.01 ug/L (Figure 3 and Appendix D). In the case of dichlobenil and pentachlorophenol, the 50% line (median) crosses the log-normal distribution at 0.025 ug/L and 0.05 ug/L, respectively.

## Parameters Sampled Only In Sediment/Storm Solids

For most organic parameters in the sediment fraction there are so few data points in this interim database that an in-depth analysis was not conducted. These sediment results are tentative because they are based on 15 or fewer samples. Results are reported per dry weight fraction.

#### Total Solids, Total Volatile Solids, and Total Organic Carbon

Total solids (called percent solids by most laboratories) is the percent of a sediment grab sample that is solid material. Storm sediment percent solids range from 0.2 to 70.7%. The low end of this range has three questionable values of 0.2, 2, and 3.3%. This means the sample was 99.8, 98, and 96.7% water. These values are questionable and should be reviewed in greater depth for the final report. The variability shown for total solids is more likely to be a result of both sampling bias and, to a lesser extent, stormwater variability. These three questionable data points will carry through most of the other sediment parameters results. This is because the percent solids value is used to normalize sediment chemistry (metals and organics) results to the solids portion of that grab sample.

No results for total volatile solids (TVS) are contained in this interim database.

Total organic carbon (TOC) in stormwater sediments ranged from 7.5 to 68% by weight. The median value was 11%. TOC analysis does not differentiate between natural carbon sources (leaves) or manmade sources (oil and fuel).

#### Polychlorinated biphenyls (PCBs)

PCBs are persistent organic pollutants used from the early 1900s to 1979 when Congress banned domestic production in the United States, although some closed system uses (transformers) and inadvertent production continues (pigments). EPA has classified PCB Aroclors as probable human carcinogens, and placed them on the priority pollutant list (EPA Priority Pollutants website, accessed 2013):

- PCB–1016 (Aroclor 1016)
- PCB–1221 (Aroclor 1221)
- PCB–1232 (Aroclor 1232)
- PCB–1242 (Aroclor 1242)
- PCB–1248 (Aroclor 1248)
- PCB–1254 (Aroclor 1254)
- PCB-1260 (Aroclor 1260)

PCB Aroclor 1254 was found to be a Case A parameter and Table 13 presents summary statistics. The remaining PCB Aroclors samples (only 7) were Case B and C parameters, and the data ranges are presented in Table 17. Each individual PCB data sheet is presented in Appendix D.

#### Semivolatile organics

Phase I permittees monitored for phenolics using EPA method 8270D which includes a longer list of semivolatile organics. These semi-volatile organics are often termed *BNAs* which stands for base, neutral, or acid-extractable semivolatile compounds. The semivolatile compounds summarized by this study were limited to the following compounds:

- 2,4,5-Trichlorophenol
- 2,4,6-Trichlorophenol
- 2,4-Dichlorophenol
- 2,4-Dimethylphenol
- 2,4-Dinitrophenol
- 2-Chlorophenol
- 2-Nitrophenol

- 4,6-Dinitro-2-methylphenol
- 4-Chloro-3-methylphenol
- 4-Nitrophenol
- o-Cresol
- Pentachlorophenol
- p-Cresol

Nine semivolatile parameters in storm sediments were completely undetected (Table 17). In contrast, phenol and p-cresol were detected more than 50% of the time (Case A, Table 13), despite small sample sizes (10 and 7, respectively). The median concentration of phenol and p-cresol in stormwater sediments is 160 ug/Kg and 170 ug/Kg, respectively.

The remaining semivolatile parameters had both small sample numbers and lower detection frequencies and are categorized as Case B and C parameters. Since all of the sediment results are based on such low sample numbers, these interim results are tentative and likely to change in the final report.

# Rainfall, Runoff, and Loading Estimates

Not enough data was provided for any meaningful summaries of storm-event rainfall or of runoff volumes. Ecology received precipitation and flow volumes for this interim findings study from only two permittees. The complete data set will be evaluated in the final report.

# Discussion

Accurately monitoring chemical concentrations in stormwater, a highly episodic and variable environment, is a formidable challenge. Washington State's Phase I permittees have spent considerable time and resources to collect a large data set of stormwater samples. In terms of number of storms, the summary statistics of this interim report far exceeds any other discharge-based or grab sample data collected previously in Washington.

# Data Limitations and Guidelines for Interpretation

# Data Quality and Sources of Error

In any environmental study, errors can occur at many different steps in the process, including:

- Sample collection
- Sample handling
- Transportation
- Sample receipt and storage at the laboratory
- Sample work up
- Sample analysis
- Data entry
- Data manipulation
- Data reporting

Since this report is a summary of third party-collected data, there is a limit to the evaluation of error or bias that can be reasonably pursued. Permittees prepared QA Project Plans and annual monitoring reports. Ecology's QA Officer reviewed and approved the QA Project Plans prior to monitoring.

#### Field Measurement Quality Objectives

Permittees are believed to have collected samples according to their Ecology approved QA Project Plans. Data reported to Ecology are believed to be useable for this summary analysis.

Site locations were chosen by permittees to represent certain land uses. Table 2 presents land use information. Few of the land use areas exclusively contain one land use. The urban and suburban landscape is rarely divided up into single land use drainage basins. Each monitored basin represents a mix of land uses and activities. For example, even though a basin may be characterized as representing 100% residential land use, the basin may have contained 80% residential and 20% commercial. Pollutants were generally greatest from the commercial and industrial land uses and lowest for low-density residential land uses. The mix of activities in any given basin will likely impact stormwater concentrations. For example, for any monitored commercial area, the extent of low-density residential also in that basin will likely bias results lower than a completely commercial basin of equal size.

#### Laboratory Measurement Quality Objectives

Standard laboratory chemical error is estimated to range from 5 to 20% for most analyses, potentially higher for trace chemicals (APHA et al., 2005).

#### Variability

Data used in this report exhibit many of the features normally expected in environmental data, such as outliers, positive skewness, non-normal distributions, seasonal patterns and censoring (non-detects). Despite the variability observed, these data are believed to represent stormwater event concentrations as defined by the permit. Ecology believes the samples do reflect stormwater concentrations because they were collected under a well-described sampling program. The permit required stormwater samples to be collected by flow-weighted compositors. Multiple authors consider composite samples superior to grab samples for estimating stormwater event mean concentrations (Ecology, 2009; FHA, 2001; SSFL, 2008; Geosyntec, 2009). Any bias or error associated with targeting the first 24 hours of the hydrograph is believed to be less than the bias or error produced from grab sampling randomly throughout the hydrograph.

One indication of the high data quality for this study is that many of the measured parameters are close to log-normally distributed. Since these data were collected and analyzed by multiple permittees and laboratories, it is encouraging to see that an overall combined data set is following a pattern similar to previous studies by other researchers (Maestre et al., 2004; EPA, 1983).

Ecology would like to investigate with permittees a few of the outlier parameter results contained in this database if they re-occur in the final compilation. Sample means are a primary interest for this report. However, outliers can have a dramatic impact on sample means and therefore can impact decisions made from this study. Therefore, Ecology wants to take steps to ensure that these outliers were not caused by errors in the field or the laboratory or during data analysis.

## Suitability for All of Western Washington

Concentrations monitored under the Phase I Permit, as represented by this interim report, reflect a range of results by land uses that can be applied to western Washington for urban and suburban stormwater discharges. (Permittees monitored large and small drainages.) The reader should recall that this interim report lacks data collected by King and Pierce Counties. The final report will increase the suitability of this data set's use throughout western Washington. Both concentration ranges and summary statistics are useful for stormwater managers, when applied to loading estimates, management strategies, cleanup, or restoration.

# **Summary of Key Patterns**

Since this report is an interim evaluation of an incomplete data set, an extensive evaluation of patterns from the data was not undertaken. A final report will be produced in 2014 that will document that effort on the complete data set.

## Non-Detected Parameters

#### **Insoluble Organics**

Some parameters measured in this study had a high proportion of non-detects, especially insoluble organic compounds. Phase I permittees monitored stormwater for multiple organic contaminants in surface runoff to identify those with a land use relationship. Table 18 lists the parameters that were detected in none or fewer than 10% of the samples collected. These parameters were largely organic pollutants such as semi-volatiles, phthalates, pesticides or PAHs. Many organic compounds tend to adsorb to solids, making them easier to detect in the sediments.

It is common that the more volatile or more easily degraded (low molecular weight) chemicals are not found in weathered samples. It is unlikely that monitoring costs would be reduced by removing a limited number of insoluble organics from the monitoring list, since the non-detected parameters from the 8270D analytical list are measured at no additional fee to the permittees.

However, for parameters that require a separate sample for a different extraction method, eliminating those parameters may reduce costs. For example, several pesticides were not found in stormwater or stormwater sediments. In particular, malathion, diazinon, and chlorpyrifos were poorly detected in both water and sediment. Also, prometon was not found in stormwater.

#### **Soluble Organics**

Some water soluble compounds also showed a high proportion of non-detects. The BTEX compounds were all listed in Table 18. This indicates that these four parameters are not found in stormwater, either because they are infrequent contaminants or because they volatilize prior to sampling. However, these BTEX results come from only one permittee for these interim findings, so these results may change. If this pattern is evident in the final report, dropping BTEX from stormwater monitoring programs will save on monitoring costs.

#### **Analysis of High Frequency Non-Detects**

For parameters with a high proportion of non-detects, data analysis was limited to reporting the range of detected concentrations. For example, there is too much uncertainty in these cases to calculate the mean and median. High frequencies of non-detected parameters were categorically treated by these findings as Case C, and not much effort was spent evaluating them. Based on Helsel's guidance, reporting the range of data is the only valid statistical approach.

Once all of the data is compiled, the frequency of non-detections will be re-evaluated. At that time, additional recommendations for stormwater monitoring parameter lists, or revised methods or method detection limits may be made.

## Seasonality

Few parameters showed an inter-seasonal pattern. Western Washington typically experiences overlapping, low intensity rains that span three of the seasons (fall, winter, and spring). The summer season includes June which is often a fairly wet month. Seasonal signals in the concentrations of parameters are believed to be suppressed by our frequent small storms. Based on the median values as shown in the box plots by season on each data sheet (Appendix D), the following parameters appear to have seasonal aspects, although these tentative results have not been statistically tested.

- *Summer higher concentrations*: fecal coliform, BOD, hardness, nitrite-nitrate, total Kjeldahl nitrogen, ortho-phosphate, total phosphorus, copper dissolved, zinc dissolved, diesel range hydrocarbons, heavy fuel oil, and heavy oil range hydrocarbons.
- *Summer low values*: Turbidity, precipitation, sample-event flow, storm-event flow.
- Fall high concentrations: lube oil and motor oil.

More statistical evaluations of the wet vs. dry season and the calendar seasons are planned for the final report. Of interest for a seasonal evaluation in the final report is the question of whether stormwater management strategies to limit build-up over the summer months will reduce the wash-off or "first flush" of contaminants into receiving waters.

### Land Use Patterns

Based on this interim report a few tentative patterns in land uses were noticed. These results may change with additional data. To examine differences among the four land use types, we examined box-plots and also applied the non-parametric Peto-Prentice test. Based on the box plots (Appendix D) for those parameters in Table 9, the range of results and median concentrations show stormwater from commercial and industrial areas have higher concentrations of contaminants than the residential uses in most cases. The noted exceptions are nitrite-nitrate and ortho-phosphate concentrations, which are higher in stormwater discharges from low-density residential areas than commercial and industrial areas. Also stormwater values for chloride and conductivity from industrial and low-density residential areas were higher than values from high-density residential areas.

Stormwater concentrations for the parameters in Table 19 were found to be statistically different between the land uses monitored. Since this interim report is based on only one-half of the anticipated data, statistical testing was limited to the most robust parameter data. No conclusions are inferred for parameters with lower sample numbers or higher frequency of censoring. An indication of land use effects is all that was sought for this interim evaluation. This decision was made to limit premature conclusions and premature management actions based on this interim assessment report.

Further analyses on log-normal parameters (such as land use or seasonal effects) should be pursued using parametric (model based) statistics that will offer more power to differentiate between groups of data. Parametric statistics can produce more accurate and precise estimates for data that meet the test assumptions. To reach accurate conclusions, we must know whether the data follow a model distribution (parametric) or do not follow a model (non-parametric). Summary statistics for each parameter by land use will be tabulated in the final report.

# Summary

This interim assessment report represents an initial analysis of a subset of the data collected under the 2007-2012 NPDES Phase I Municipal Stormwater Permit, under Special Condition S8.D. The permittees are all located in western Washington. The goals of this interim report were to compile the permittees' data, develop statistical approaches to summarize the data, and begin to develop a regional baseline characterization of stormwater quality. Permittees collected a large amount of highly representative storm-event data under a coordinated monitoring program and using flow-weighted automated compositors. Data represent stormwater discharges from multiple land uses and across storm, seasonal, and annual timeframes.

This report considered an estimated 40-60% of the stormwater outfall data collected under S8.D. Despite evaluating only one-half of the data, this report presents valid statistical tests for multiple reporting limits and non-detect data, as well as some tentative results from the largest known collection of stormwater monitoring data in Washington.

These interim findings are based on analysis of 22,049 data records submitted to Ecology by the permittees, representing an estimated 283 storms. Up to 85 chemicals were analyzed for any given stormwater sample, and 67 chemicals were analyzed in stormwater sediment samples. Compiling data from multiple sources was challenging, due to different parameter names, sample fractions, or units reported. This placed limitations on Ecology's understanding of the compiled data. Some, but not all, of these challenges were addressed in these findings.

Very few rainfall or flow records were provided with the interim data; therefore, no analyses of rainfall depth, storm or sample volumes, or pollutant loads were conducted. Ecology hopes to conduct these analyses in the 2014 final report.

Plots were made of the data and summary statistics (e.g., mean and median were calculated using techniques that correctly include non-detect values). This interim study evaluated the data by land use and season for parameters with detection frequencies of 50% or greater. Parameters with less than one-half of the data as reported as detects were summarized by data ranges. All parameters will be re-evaluated in the final report.

# Conclusions

Following are the major conclusions from this interim study. A final report in 2014 will present conclusions based on all of the 2007-2012 stormwater characterization monitoring data.

- A total of 32 chemicals were detected infrequently, and 19 chemicals were not detected at all. The non-detected chemicals included BTEX, many of the pesticides, and an assortment of organic compounds.
- Pollutant concentrations in stormwater for the majority of the Case A (well detected) parameters were generally highest from basins with commercial and/or industrial land uses. These results agree with national stormwater characterization studies: National Urban Runoff Program (EPA, 1983) and National Stormwater Quality Database (Maestre et al., 2004).
- Pollutant concentrations in stormwater were greater than the instream storm-flow concentrations measured by the *Toxics in Surface Runoff Study* (Herrera, 2011) for all parameters, except nitrite-nitrate and turbidity.
- The significance of one or more land uses was evaluated for each parameter. We tentatively found that stormwater concentrations from industrial areas are highest for some conventionals (chloride, hardness, conductivity, surfactants, turbidity, fecal coliform, total phosphorus) and metals (copper, cadmium, lead, zinc). Statistical comparisons between each of the four land uses were not performed on the interim results.
- This interim assessment found stormwater concentrations from commercial areas are highest for some conventionals (total suspended solids, BOD, total Kjeldahl nitrogen), petroleum hydrocarbons, dissolved lead, and some organics (e.g., bis(2-ethylhexyl) phthalate, pyrene).
- This assessment found stormwater concentrations from low-density residential areas were highest for nitrite-nitrate and ortho-phosphate.
- A seasonal first-flush effect may occur for several parameters found to have high concentrations during the summer. These parameters include all the nutrients measured, fecal coliform, BOD, copper, zinc, and total petroleum hydrocarbon (TPH). The 2014 final report will evaluate this further.

# **Recommendations**

Based on the preliminary findings of this interim analysis, the following recommendations are made.

- Ecology should compile all of the stormwater data collected under S8.D (when available) from Ecology's EIM database. Analyses should include, at a minimum, the six plots discussed in the interim report because they appropriately handle multiple non-detected thresholds values.
- Final S8.D results should include rainfall and flow volume analysis. Pollutant loads may be evaluated for the sampling, storm, and seasonal timeframes.
- Ecology should conduct a more in-depth review of the reporting-limit thresholds to be certain that the S8.D data were all reported at the same quantitation level. Ecology should also review the different laboratory methods to be certain the results are comparable.
- Ecology should investigate with permittees the few anomalous results in the S8.D data set to ascertain whether these data should be qualified differently, if these data occur in the final data set.
- Ecology should evaluate the S8.D data for patterns among parameters that could help identify sources of pollution to stormwater.
- For the 2014 final report, rigorous statistical techniques for both non-parametric and parametric data sets should be employed to evaluate both land use and seasonal signals. Ecology should compare the results among the land uses and seasons and define a timeframe for testing the seasonal first flush.
- Ecology may consider conducting a separate investigation of the effect of substitution for non-detect results on a subset of the results from the permittees' S8.D data to support a better comparison with other regional and national stormwater studies.
- Ecology should consider updating the Northwest Total Petroleum Hydrocarbon (NWTPH) method to eliminate discordant summation techniques and provide specific reporting requirements.

# References

# Websites

ATSDR <u>www.atsdr.cdc.gov/</u>

Comprehensive R Archive Network (CRAN) http://cran.r-project.org/

Ecology's Sediment Phthalate Work Group www.ecy.wa.gov/programs/tcp/smu/phthalates/phthalates\_hp.htm

Ecology's Control of Toxics Chemicals in Puget Sound www.ecy.wa.gov/programs/wq/pstoxics/index.html

EPA's NPDES Stormwater "Frequently Asked Questions" <u>http://cfpub.epa.gov/npdes/faqs.cfm?program\_id=6</u>

EPA's Priority Persistent Bioaccumulative and Toxic Profiles www.epa.gov/pbt/pubs/cheminfo.htm

EPA's Priority Pollutants <u>http://water.epa.gov/scitech/methods/cwa/pollutants.cfm</u>

NOAA's National Atmospheric Deposition Program NTN Maps by Analyte <u>http://nadp.sws.uiuc.edu/ntn/annualmapsbyanalyte.aspx</u>

# **References Cited in Text**

Antweiler, R.C. and Taylor, H.E., 2008. Evaluation of Statistical Treatments of Left-Censored Environmental Data using Coincident Uncensored Data Sets: I. Summary Statistics. Environmental Science & Technology, v. 42, p. 3732-3738.

APHA, 2005. Standard Methods for the Analysis of Water and Wastewater, 21<sup>st</sup> Edition. Joint publication of the American Public Health Association, American Water Works Association, and Water Environment Federation. <u>www.standardmethods.org/</u>

Burton, G.A. Jr., and R. Pitt, 2002. Stormwater Effects Handbook: A Tool Box for Watershed Managers, Scientists, and Engineers. CRC Press, Inc., Boca Raton, FL. 911 pgs.

Clarke, J.U., 1998. Evaluation of censored data methods to allow statistical comparisons among very small samples with below detection limit observations. *Environmental Science & Technology*, v. 32, pp. 177-183.

Cohen, A.C., 1959. Simplified estimators for the normal distribution when samples are singly censored or truncated. Technometrics, v. 1, pp. 217-237.

Cohen, A.C., 1976. Progressively censored sampling in the three parameter log-normal distribution. Technometrics, v. 18, pp. 99-103.

Ecology, 1992. Statistical Guidance for Ecology Site Managers, Publication No. 92-54, August 1992. <u>https://fortress.wa.gov/ecy/publications/SummaryPages/9254.html</u>

Ecology, 1993. Supplement S-6 to Statistical Guidance for Ecology Site Managers, Analyzing Site or Background Data with Below-Detection Limit or Below-PQL Values (Censored Data Sets). Washington State Department of Ecology, Olympia, WA.

Ecology, 1997. Analytical Methods for Petroleum Hydrocarbons. Washington State Department of Ecology, Olympia, WA. June 1997. Publication No. 97-602. https://fortress.wa.gov/ecy/publications/SummaryPages/97602.html

Ecology, 2006. Fact Sheet for National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permit for Discharges from Large and Medium Municipal Separate Storm Sewers. Washington State Department of Ecology, Olympia, WA. March 22, 2006.

www.ecy.wa.gov/programs/wq/stormwater/municipal/phaseIpermit/phifinalfs.pdf

Ecology, 2007. Phase I Municipal Stormwater Permit: National Pollutant Discharge Elimination System and State Waste Discharge General Permit for Discharges from Large and Medium Municipal Separate Storm Systems. Issued January 17, 2007. Last Modification September 1, 2010. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/programs/wq/stormwater/municipal/phaseIpermit/MODIFIEDpermitDOCS/Ph aseIStormwaterGeneralPermit.pdf

Ecology, 2009. Standard Operating Procedure for Automatic Sampling for Stormwater Monitoring, Version 1.0, Washington State Department of Ecology, Olympia, WA. September 16, 2009. SOP No. EAP002. <u>www.ecy.wa.gov/programs/eap/quality.html</u>

Ecology, 2011. Standard Operating Procedure for Statistical Treatment of Nondetects in Environmental Monitoring Data. Unpublished draft dated July 7, 2011.

EPA, 1983. Results of the Nationwide Urban Runoff Program. Volume I – Final Report. U.S. Environmental Protection Agency, Water Planning Division, PB 84-185552, Washington, D.C. 20460. December 1983.

EPA, 1998. Total vs. Total Recoverable Metals. Memorandum from William A. Telliard, Director of Analytical Methods Staff for the Engineering and Analysis Division. U.S. Environmental Protection Agency. Dated August 19, 1998.

EPA, 2006. Data Quality Assessment: Statistical Methods for Practitioners, Office of Environmental Information, U.S. Environmental Protection Agency. EPA QA/G-9S.

EPA, 2008. Polycyclic Aromatic Hydrocarbons (PAHs)--EPA Fact Sheet. U.S. Environmental Protection Agency, Office of Solid Waste, January 2008. www.epa.gov/osw/hazard/wastemin/minimize/factshts/pahs.pdf EPA, 2009. Statistical Analysis of Groundwater Data at RCRA Facilities, Office of Resource Conservation and Recovery, U.S. Environmental Protection Agency. EPA 530-R-09-007.

Federal Highway Administration (FHA), 2001. Guidance Manual for Monitoring Highway Runoff Water Quality, Federal Highway Administration, D.C. June 2001.

Geosyntec Consultants and Wright Water Engineers, Inc. 2009. Urban Stormwater BMP Performance Monitoring. Sponsored by Water Environment Research Foundation, U.S. Environmental Protection Agency, Federal Highway Administration, and American Society of Civil Engineers – Environmental Water Resources Institute. October 2009.

Helsel, D.R., 2005. Nondetects and Data Analysis; Statistics for Censored Environmental Data, John Wiley & Sons, Inc., NJ, 250 p.

Helsel, D.R., 2012. Statistics for Censored Environmental Data Using Minitab® and R. Second Edition. John Wiley & Sons, Inc., NJ, 342 p.

Helsel, D.R. and Cohn, T.A., 1988. Estimation of Descriptive Statistics for Multiply Censored Water Quality Data, Water Resources Research, v. 24 (12), pp. 1997-2004.

Herrera Environmental Consultants, Inc., 2011. Control of Toxic Chemicals in Puget Sound: Phase 3 Data and Load Estimates. Washington State Department of Ecology, Olympia, WA. May 2011. Publication No. 11-03-010. https://fortress.wa.gov/ecy/publications/publications/1103010.pdf

Hirsch, R.M. and Stedinger, J.R., 1987. Plotting positions for historical floods and their precision. Water Resources Research, v. 23, pp. 715-732.

Lee, Lopaka, 2012. NADA: Non-detects And Data Analysis for environmental data. R package version 1.5-4. <u>http://CRAN.R-project.org/package=NADA</u>

Lombard, S. and C. Kirchmer, 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030. <u>www.ecy.wa.gov/biblio/0403030.html</u>.

Lubliner, B., 2012. Quality Assurance Project Plan: Phase 1 Municipal Stormwater Permit Data Review. Washington State Department of Ecology, Olympia, WA. Publication No. 12-03-125. https://fortress.wa.gov/ecy/publications/SummaryPages/1203125.html

Maestre, A., Pitt, R.E., and Derek Williamson, 2004. Nonparametric statistical tests comparing first flush with composite samples from the NPDES Phase 1 municipal stormwater monitoring data. Stormwater and Urban Water Systems Modeling. Pp. 317–338 *In:* Models and Applications to Urban Water Systems, Vol. 12. W. James (ed.). Guelph, Ontario: CHI (www.unix.eng.ua.edu/~rpitt/Publications/Stormwater%20Characteristics/first%20flush%20Mae stre%20and%20Pitt%20James%202003.pdf)

Maestre, A. and R. Pitt, 2005. The National Stormwater Quality Database, Version 1.1, A Compilation and Analysis of NPDES Stormwater Monitoring Information. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.

Maestre, A., R. Pitt, S. R. Durrans and S. Chakraborti, 2005. Stormwater Quality Descriptions using the Three Parameter Lognormal Distribution. 2004 Stormwater and Urban Water Systems Modeling Conference pp. 247-274, Toronto, Ontario, Canada. <u>Effective Modeling of Urban Water Systems, Monograph 13</u>

Microsoft, 2007. Microsoft Office XP Professional, Version 10.0. Microsoft Corporation.

Newman, M.C., Dixon, P.M., and Pinder, J.E., 1990. Estimating mean and variance for environmental samples with below detection limit observations. *Water Resources Bulletin*, v. 25, pp. 905-916.

Pitt, R., 2011. The National Stormwater Quality Database, Version 3.1. Summary for EPA. http://rpitt.eng.ua.edu/Publications/4\_Stormwater\_Characteristics\_Pollutant\_Sources\_and\_Land \_\_\_\_\_\_Development\_Characteristics/Stormwater\_characteristics\_and\_the\_NSQD/NSQD%203.1%20s ummary%20for%20EPA%20Cadmus.pdf

R Core Team, 2012. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. <u>www.R-project.org/</u>.

Singh, A., Singh, A., and Iaci, R.J., 2002. Estimation of Exposure Point Concentration Term using a Gamma Distribution. EPA/600/R-02/084, October 2002.

Singh, A., Maichle, R., and Lee, S., 2006. On the computation of a 95% upper confidence limit of an unknown population mean based upon data sets with below detection limit observations. EPA/600/R-06/022, March 2006.

SSFL CDO Expert Panel, 2008. Sample Collection Methods for Runoff Characterization at Santa Susana Field Laboratory (SSFL), Santa Susana, CA, October 20, 2008.

Van Metre, P.C., Mahler, B.J., Scoggins, M., and Hamilton, P.A., 2006. <u>Parking lot sealcoat-A</u> <u>major source of polycyclic aromatic hydrocarbons (PAHs) in urban and suburban environments</u>: U.S. Geological Survey Fact Sheet 2005-3147, 4 p.

# **Appendices**

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## Appendix A. Permittees' Quality Assurance Project Plans

Website Link to QA Project Plans on file with Ecology

www.ecy.wa.gov/programs/wq/stormwater/municipal/s8dswmonitoring.html

#### Snohomish County

Quality Assurance Project Plan (QAPP) Stormwater Characterization Monitoring S8.D Final. December 2008. Prepared by Snohomish County Public Works, Surface Water Management Division, 3000 Rockefeller Ave, Everett, WA 98201.

#### King County

Quality Assurance Project Plan for King County Stormwater Monitoring Under the NPDES Phase 1 Municipal Permit WAR04-4501 (Issued February 2007). Updated November 2010. King County Department of Natural Resources and Parks, Water and Land Resources Division, Science Section. King Street Center, KSC-NR-0600, 201 South Jackson Street, Suite 600, Seattle, WA 98104.

#### Pierce County

Quality Assurance Project Plan for Pierce County Phase I Municipal Stormwater NPDES Permit Section S8.D – Stormwater Characterization. November 5, 2009. Prepared for Pierce County Surface Water Management, 2702 South 42<sup>nd</sup> Street, Suite 201, Tacoma, WA 98409-7322. Prepared by Herrera Environmental Consultants.

#### Clark County

Quality Assurance Project Plan for Stormwater Characterization Monitoring. Conducted Under Section S8.D of the Phase I Municipal Stormwater Permit by Clark County. Prepared by U.S. Geological Survey, Oregon Water Science Center. Revised March 2011 by Clark County Department of Environmental Services, Clean Water Program, Vancouver, WA.

### City of Tacoma

Section S8.D - Stormwater Characterization Quality Assurance Project Plan, Phase I Municipal Stormwater NPDES Permit, Permit No.: WAR04-4003. Revision: S8.D-003 (Final). Revision Date: 08/16/2009. City of Tacoma, Tacoma, WA.

### City of Seattle

Section S8.D - Stormwater Characterization Quality Management System Planning Document, Quality Assurance Project Plan. NPDES Phase I Municipal Stormwater Permit, Permit No.: WAR04-4503. Revision: R2D0 (Final). Draft revised: 03/31/2011.

### Port of Tacoma

Quality Assurance Project Plan for Stormwater Monitoring Conducted Under the Phase I Municipal Stormwater Permit by Port of Tacoma. Final August 2009.

#### Port of Seattle

Quality Assurance Project Plan for Stormwater Monitoring Conducted Under Section S8.D of the Phase I Municipal Stormwater Permit. Addendum #1. November 2011. Port of Seattle Marine Division. Prepared by TEC Inc. and Otak, Inc. for Port of Seattle.

Quality Assurance Project Plan for Stormwater Monitoring Conducted Under Section S8.D of the Phase I Municipal Stormwater Permit. February 20, 2009. Port of Seattle Marine Division. Prepared by TEC Inc. and Otak, Inc. for Port of Seattle.

# Appendix B. Parameters and Laboratory Methods

Parameter	Laboratory	y Methods Used									
Conventionals	NoValue	EPA405.1	SM5210B								
BOD	124	57	123								
	NoValue	EPA300.0	EPA325_2	SM4500CL-B							
Chloride	152	170	4	2							
	NoValue	EPA120.1									
Conductivity	194	179									
	NoValue	EPA200.7	SW6010B								
Hardness as CaCO <sub>3</sub>	193	123	57								
	NoValue	EPA150.1									
pH	115	51									
	NoValue	SM5540C									
Surfactants	168	179	-								
	NoValue	PLUMB81TC	SW9060								
Total Organic Carbon		7	8	-							
	NoValue	EPA160.3	SM2540B								
Total Solids		7	11								
	NoValue	EPA160.2	SM2540D								
Total Suspended Solids	185	57	123								
	NoValue	EPA180.1	SM2130B-F								
Turbidity	108	57	121								
	NoValue	SM9221B	SM9221C	SM9222D							
Fecal Coliform	84	112	5	75							
Nutrients	NoValue	EPA351.2	EPA351_4	EPA353_2							
Nitrite-Nitrate	159			180							
Total Kjeldahl Nitrogen	159	172	8								
	NoValue	EPA365.2	SM4500PE	SM4500PF							
Ortho-phosphate	161	18	122								
Total Phosphorus	154	57	88	35							
Metals	NoValue	EPA200.8	EPA200.7	SW6010B							
Cadmium	392	369		8							
Copper	389	370		8							
Lead	386	370		8							
Zinc	386	370		8							
Magnesium			122	57							
	NoValue	EPA200.7	EPA245.1	SW7470A	SW7471A	SW7471A	SW7471A S	SW7471A SW	SW7471A SW74	SW7471A SW747	SW7471A SW7471
Mercury	285	1	98	80	5	5	5	5	5 3	5 3	5 3

 Table B-1. Number of records by parameter for each analytical method used.

Parameter	Laborator	y Methods Us	ed			
BTEX	EPA624					
Benzene	120					
Ethylbenzene	120					
Toluene	120					
Total Xylenes	120					
		NWTPH-				
Petroleum Hydrocarbons	NoValue	GX	NWTPH-DX			
Gasoline Range Hydrocarbons	126	191				
Diesel Range Hydrocarbons	116		191			
Heavy Fuel Oil			119			
Heavy Oil Range Hydrocarbons	116					
Lube Oil			27			
Motor Oil			44			
Pesticides	NoValue	SW8270D	SW8270DSIM	SW8270M		
Chlorpyrifos	189	123	71			
Diazinon	189	123	71			
Dichlobenil	188	127	47	5		
Malathion	189	123	71			
Pentachlorophenol	165	127	72			
Prometon	189	126	47	5		
Simazine		1				
	NoValue	SW8150	SW8151	SW8151A	SW8321	SW8321B
2,4-D	166	5	123	36		22
Mecoprop	167	5	123	36		22
Triclopyr	166		123	5	5	43
SVOC	NoValue	SW8270D	SW8270DSIM	SW9065		
2,4,5-Trichlorophenol		4	3			
2,4,6-Trichlorophenol		4	3			
2,4-Dichlorophenol		4	3			
2,4-Dimethylphenol		4	3			
2,4-Dinitrophenol		4	3			
2-Chlorophenol		4	3			
2-Methylnaphthalene	191	123	72			
2-Nitrophenol		4	3			
4,6-Dinitro-2-Methylphenol		4	3			
4-Chloro-3-Methylphenol		4	3			
4-Nitrophenol		4	3			
o-Cresol		4	3			
p-Cresol		4	3			
Phenol		4	3	3		

## Table B-1 (cont'd). Number of records by parameter for each analytical method used.

Parameter	Laboratory		
Phthalates	NoValue	SW8270D	SW8270DSIM
Bis(2-ethylhexyl) phthalate	189	185	8
Butyl benzyl phthalate	189	187	8
Dibutyl phthalate	189	187	8
Diethyl phthalate	191	187	8
Dimethyl phthalate	191	187	8
Di-N-Octyl Phthalate	189	187	8
РАН	NoValue	SW8270D	SW8270DSIM
1-Methylnaphthalene		67	70
Acenaphthene	190	123	72
Acenaphthylene	191	123	72
Anthracene	191	123	72
Benz[a]anthracene	189		64
Benzo(a)pyrene	189	123	72
Benzo(b)fluoranthene	78	123	30
Benzo(g,h,i)perylene	189	123	64
Benzo(k)fluoranthene	78	123	30
Chrysene	189	123	72
Dibenz[a,h]anthracene	189	123	72
Dibenzofuran	78		64
Fluoranthene	189	123	72
Fluorene	191	123	72
Indeno(1,2,3-cd)pyrene	190	123	72
Naphthalene	189	123	72
Phenanthrene	190	123	72
Pyrene	189	123	72
РСВ	SW8081	SW8082	
PCB-Aroclor 1016	2	6	
PCB-Aroclor 1221	2	6	
PCB-Aroclor 1232	2	6	
PCB-Aroclor 1242	2	6	
PCB-Aroclor 1248	2	6	
PCB-Aroclor 1254	2	6	
PCB-Aroclor 1260	2	6	

## Table B-1 (cont'd). Number of records by parameter for each analytical method used.

# Appendix C. Description of the Six Statistical Plots

This appendix describes each of the six plots created for data analysis. Four parameters are displayed and described for each of the six plot types. The four parameters are fecal coliform bacteria, total phosphorus, dissolved copper, and 2,4-D (an herbicide). These parameters were selected because they display a variety of discussion elements, considerations for data summaries, and peculiarities encountered in this interim report. For both the jitter and box plots, the x-axis is categorical and uses the abbreviations defined below:

### Land Uses

Ind	= Industrial
Com	= Commercial
HRes	= High-Density Residential
LRes	= Low-Density Residential

### Sample Result

Det = Count of detected records ND = Count of non-detected records and the percent non-detected records of the total

## Season Type

- Winter = Winter Quarter (January, February, March)
- Spring = Spring Quarter (April, May, June)
- Summer = Summer Quarter (July, August, September)
- Fall= Fall Quarter (October, November, December)
- Dry Seas = Dry Season (May 1 through September 30)
- WetSeas = Wet Season (October 1 through April 30)

## 1. Jitter Plot

Jitter plots offer an excellent visual of the data. The jitter plot (Figure C-1) shows both the detected data as points and the non-detected data as bars extending from zero to provided reporting limit. The bar is useful in conveying the idea that we do not know the true value of the non-detect, only the range for which its true value occurs. The two-toned purple dots are the detected data points, divided into dry and wet seasons.

The jitter plots are divided into four vertical panels. Each panel represents a different land use type. Within each panel, the x-values are randomized (jittered) to spread the data out and make them easier to view. Land use types are indicated by abbreviations below the x-axis, along with the number of detects, the number of non-detects, and the percentage of data censored.

As seen in the jitter plots, most of the data for fecal coliform, total phosphorus, and dissolved copper were detected values, whereas the majority of the data for 2,4-D were non-detects as indicated by the gray lines.

The fecal coliform jitter plot shows that the data spans 5 orders of magnitude and includes non-detects.



Figure C-1. Jitter plots for four example parameters.

The total phosphorus data range from 0.01 to 1 mg/L. There are at least three non-detects at elevated reporting limits. The reason for these elevated non-detects is unknown. This could be due to matrix interference, or this could illustrate a gap in the data QA process (QA) at the laboratory or the data review level. Ecology did not investigate peculiarities such as these for two reasons: (1) The data had already been QA reviewed by the laboratory and the permittees and therefore were useable for summarization into the regional data set, and (2) time was limited under the grant process to investigate a small number of oddities.

The dissolved copper jitter plot shows the bulk of the detections are from 1 to 79 ug/L. Similar to total phosphorus, there are three non-detects reported at elevated reporting limits. This may be due to matrix interferences or gaps in the data review. The other 4 to 5 non-detects are shown at a reporting limit of 0.1 ug/L.

Finally, the jitter plot for 2,4-D shows that the bulk of the data were non-detect. Only the highdensity residential land use approached a 50% detection rate. Organic contaminants in stormwater were more likely to contain greater percentages of non-detects than conventional parameters, nutrients, or metals. Additionally, non-detects for organics were more likely, as shown for 2,4-D, to have multiple reporting limits for non-detects. The variable reporting limits may be due to the interfering matrices, low sample volumes, or different laboratory QA processes. An inter-laboratory comparison for the analytical methods used under the S8.D monitoring programs in the Puget Sound Region has not been investigated to Ecology's knowledge.

## 2. Probability Plots

Some statistical calculations assume that data follow a specific distribution. In these cases, a method is needed to check whether this assumption is valid. For example, stormwater professionals have consistently found that the concentrations of many stormwater constituents follow a log-normal distribution (EPA, 1983; Burton and Pitt, 2002; Maestre et al., 2004, 2005). Stormwater concentrations usually have a log-normal distribution, resulting in a positive bias, resulting in the average values being larger than the median values (Pitt, 2011).

Probability plots are used to compare a data set to a specified distribution (Helsel, 2012), in this case a log-normal distribution. The distribution is represented on the plot as a straight line, and observed data are plotted as individual points. If the data points fall near the line then they are described as reasonably fitting the log-normal distribution. If the data points show curvature or have a number of points that plot far from the line, then the data are said to differ significantly from the log-normal distribution. Parameters with few or no non-detects were tested for a normal or log-normal distribution using the Shapiro-Wilk test. This was discussed further in the *Methods* section of the report.

For all other parameters, the presence of non-detects must be properly accounted for when creating a probability plot. Although non-detects are not shown on the plot, they affect the placement of the observed data points on a probability plot. A probability plot that ignores non-detected data is invalid according to Helsel (2012).

We used the "cenros" function in NADA for R to generate probability plots for this report. This function accounts for the proportion of the data below each reporting limit and adjusts the placement of the detected data accordingly.

On these plots, the lower x-axis shows the quantile while the upper x-axis the represents the percentiles of the data distribution. The y-axis shows the concentrations (typically in log scale). The detected data are shown as black dots. The non-detect values are ranked and the positional range and count of data points associated with the non-detects is taken into consideration, but are not shown on the plot.

These plots use the entire data set and do not divide the data by land use. This is particularly useful in describing stormwater baseline characterization conditions.

In the four examples above, fecal coliform is the only plot that does not appear to "fit" the straight line well. This is a visual indication that fecal coliform are not log-normally distributed.

Probability plots accurately present the median, as well as other percentiles presented on the upper x-axis of the entire data set. For example, the median values for fecal coliform, total phosphorus, and dissolved copper appear to fall at the middle point of the detected data. This makes sense, since we learned from Figure C-1 that the majority of their data were made up of detected records.

On the other hand, the median for 2,4-D is below the bulk of the detected data. This also is logical, because in Figure C-1 we learned that 76% of the 2,4-D data points were non-detect. Therefore in Figure C-2, the median value falls in the area of the plot where there are few to no data points showing.



Figure C-2. Probability plots for four example parameters.

## 3. Plots of Non-Detects

To understand differences in laboratory reporting levels, we plotted non-detect thresholds reported by the permittees. Non-detect data are shown in these plots as line segments extending from zero to the laboratory reporting level. The color of the line segment indicates which laboratory performed the analysis. Laboratory names were removed and represented by a number. The focus of this plot is not to identify permittees or their laboratories, but rather to illustrate the number of laboratories and the numerous reporting limits reported.

Within each plot, the non-detect data are spaced evenly and sorted from lowest to highest reporting level. Plots with few points show the lines distinctly, whereas plots with a large number of data points show no spaces between the lines. Examples are shown in Figure C-3.



Figure C-3. Non-detect plots for four example parameters.

These examples illustrate both the frequency a parameter was not detected and the variability in the reporting-limit threshold for the non-detect data. Recall that variability comes from different samples' matrices, sampling dates, handling techniques, and laboratories. The parameter data sheet in Appendix D did not contain this plot if there were no non-detect data.

For the final report, Ecology would like to confirm with the permittees that the threshold number given by each permittee was really the reporting limit. Because some of these threshold values are so low for some of the parameters, we suspect some of the limits may have been method detection limits or minimum levels.

## 4. Empirical Distribution Function (edf)

These plots (Figure C-4) help identify differences in concentrations among the four land use types. Edf plots of the observed data are constructed by ranking the data from smallest to largest (Helsel, 2012). Edf plots are also known as the Kaplan-Meier (KM) Curves. The graph shows the likelihood of any given sample concentration to occur in the population of the data set by percentiles. Line type and color indicates land use, as shown in the plot legend. They were created using the "cenfit" command in NADA for R.

On these plots, we swapped axes from the usual convention in order to allow comparison with the jitter plots and box plots. Only the detect values are actually plotted, but their positions are influenced by both detections and non-detections. This is a preferred method to display data sets that contain non-detects, as opposed to the traditional box and whisker plots that use only detected values. Edf plots were not shown if there were less than five detected values for any given parameter, and in this case, the data plots (Appendix D) will show the message: "Not Plotted (Less than 5 detections)".



Figure C-4. Edf plots based on KM for four example parameters.

These four example parameters begin to illustrate the impact of the surrounding land use on the water quality of stormwater.

In the case of fecal coliform, the edf curve for industrial is similar to commercial but quite different from low-density residential. A vertical dashed line was placed on the fecal coliform plot to illustrate where the median value (50%) occurs by land use. A horizontal dashed line was placed to show that fecal concentrations of 100 cfu/100 mL or higher occur approximately >95% of the time for the industrial land use, > 90% for commercial, > 35% for high-density residential, and > 65% of the time for low-density land use.

For total phosphorus, there is less difference observed among the four land use types.

For 2,4-D, the edf for high-density residential shows both a higher proportion of detections and consistently higher concentrations. The 2,4-D data sets for the other land uses are largely non-detect (> 75% of values) but also include some high concentration detections.

When many non-detects occur at the same reporting level, this shows up in the edf plot as a long horizontal line segment (e.g., 2,4-D).

## 5. Box Plot by Land Use

Standard box and whisker plots were created in R software to compare concentrations between land use types (Figure C-5). This type of box plot is described in Helsel and Hirsch (2002). The box extends from the 25<sup>th</sup> to the 75<sup>th</sup> percentile and is split with a heavy line at the 50<sup>th</sup> percentile. Whiskers extend to the last observation within 1.5 times of the box height (prior to log transformation). Observations beyond this are shown as individual hollow circles. Thus, half of the data should fall within the box, a quarter of the data should lie above the box, and a quarter of the data should lie below the box. The box plots were created using the entire data set and make no distinction between detected and non-detected values. That is, all data values were included as if they were detections.



Figure C-5. Box and whisker plots of the detected data by land use for four example parameters.

As discussed in Helsel (2012), only the portions of the box plot which lie above the maximum non-detect limit are known exactly. In order to illustrate the region where the non-detected thresholds would influence the box plots, the visual of a gray "curtain" is used to represent the range of non-detects, as if it were pulled up over the box plot to illustrate where uncertainty still remains in the data set. The box outline is dashed under the gray curtain to reflect this uncertainty. Horizontal lines also indicate the maximum and minimum non-detect thresholds.

Helsel (2012) recommends calculating the portion of the box plot using either KM or ROS statistics to estimate the  $25^{\text{th}}-50^{\text{th}}-75^{\text{th}}$  percentiles. This was not done for this report, so very little weight should be given to portions of the box plot in the shaded region. For the final report, box plot calculations may incorporate this recommendation, if time permits.

In some cases, the shaded region may be caused by only one or two non-detects. In these cases, the box plot may be only slightly affected. Each case must be assessed individually.

Similar to edf plots (Figure C-4), box plots illustrate how the surrounding land uses impact water quality of stormwater. In the case of fecal coliform, the box (25<sup>th</sup> and 75<sup>th</sup>) and median values (line) for industrial is quite different than the box for low-density residential. Visually the reader can see that the open circles range up to almost the same values, despite the land use categories. Box plots by land use were not calculated if there were less than 5 detected values for any given parameter. Data plots (Appendix D) will show the message: "Not Plotted (No land use has 5 or more detections)".

The box plot graphs and the edf plots show similar patterns for fecal coliform and total phosphorus, with industrial and commercial areas showing higher concentrations than the residential land uses. If a parameter was detected in all samples or had relatively few non-detects, then the edf and box plots will show the same information.

This is not true for parameter data sets that contain more non-detects. This is an important distinction. Unlike the edf plots, the non-detects data are not distinguished from detections in the box plot percentile calculations. For parameters where non-detects account for a larger percentages of the data set, this means that a box plot is not presenting the same information as the edfs. In other terms, the box plots are misleading for data sets that comprise medium to large percentages of non-detect data. This is the case for the dissolved copper and 2,4-D shown and is true for many of the organic parameters monitored.

For dissolved copper, the box plot shows the commercial land use has potentially higher summary statistics and outliers than the other land uses. The gray "curtain" of non-detects is pulled up higher than for any other land use. The threshold assigned to the non-detects is much higher for commercial land uses. By comparing the edf to the box plot for dissolved copper, more confidence is gained from the edf confirming that the commercial land use curve is higher than the other land uses. There is more confidence in the edf curve because the non-detects have been appropriately factored into the data set.

For dissolved copper, there appears to be a difference between the commercial stormwater concentrations and the other land uses when looking at both the edf plot (Figure C-4) and box plot (Figure C-5). The statistical difference between land uses was tested for using the Peto-

Prentice (discussed more in the following section). Notice, the industrial land use curve is quite flat and that the box plot is thin. These indicate that variability has a narrower range for dissolved copper for commercial land uses than the low residential land use. When looking at the edf for the industrial land use, we conclude with certainty that 90% of the data are above 2 ug/L. This is not known for certain looking at the box plot because the "curtain" for the industrial land use extends almost up to 5 ug/L.

The same logic is true in comparing each of the box plots to its edf curve. For example, in the edf for 2,4-D, stormwater concentrations from high-density residential areas are higher, with a higher degree of certainty. However, when looking at the box plot, the curtain of uncertainty is pulled all the way above the 75<sup>th</sup> percentile. This illustrates the limitation of showing the information using box plots for data sets with non-detects.

### 6. Box Plot by Season

These box and whisker plots (Figure C-6) are identical to the box plots by land use (Figure C-5), except that they are broken up by season. Seasons are as follows: Winter was Jan-Mar, spring was Apr-Jun, summer was July-Sept, and fall was Oct-Dec.



Figure C-6. Box and whisker plots of the detected data by season for four example parameters.

Box plots by season were not calculated if there were less than 5 detected values for any given parameter. Data plots (Appendix D) will show the message: "Not Plotted (No season has 5 or more detections)".

Ecology did not test for statistical significance of seasonal effects. This assessment will be conducted for the final data report, when all the data are available. Since non-detect thresholds are less likely to affect the highest values, the reader should look beyond the median values for

this partial data set. Despite illustrating only the detected results, these seasonal box plots give some interesting information.

Although statistical evaluations have not been conducted, the reader can see that stormwater concentrations of fecal coliform, for example, vary among the seasons. The  $75^{\text{th}}$  percentile, maximum values, and outliers are all higher for the summer and fall seasons. Note that some parameters (e.g., fecal coliforms) are plotted on log scales and some are on linear scales. Fecal concentrations are substantially higher in the summer than the winter. Also, recall that the permit defined wet and dry season based on typical hydrologic conditions in the Pacific Northwest. The wet and dry seasons do not match well with the seasons discussed in this report. The dry season captures spring and summer. The *fall quarter* starts October 1 and is considered to be part of the wet season. The earlier storms of the *fall season* may actually be the seasonal first-flush storms.

These interim findings suggest slight seasonal differences exist for some parameters (e.g., in summer for total phosphorus concentrations). Since seasonal statistical testing will wait for the complete data set, only tentative conclusions on seasonal differences can be made.

## Case C Parameter – Data Sheet

In the data plots, many of the graphs are not shown, and the message "Not Plotted (Case C)" is given. Figure C-7 gives an example data sheet for a Case C parameter, dibenzofuran.



Figure C-7. Six plots for the parameter, dibenzofuran, in stormwater.

Dibenzofuran is analyzed as part of the PAH list and is a regulated hazardous substance. Its sources include areas of creosote or coal tar use. Many of the aromatic compounds are fairly insoluble in water, and low concentrations in stormwater are anticipated. Data sets that contain a large frequency of non-detects, such as for dibenzofuran, do not have enough detected values to warrant further analysis. The three plots that give the most information about the non-detections are retained. The jitter plot shows that there were seven detected concentrations and that there were 128 non-detects. The plot of non-detect thresholds shows that many reporting limits were reported. The edf plot shows that >90% of data was non-detect, and when detections were made, they varied from 0.02 to 0.5 ug/L.

# **Appendix D. Data Plots for Parameters**

Appendix D (133 pages) is available only online.

It is linked to this report at <u>https://fortress.wa.gov/ecy/publications/SummaryPages/1303043.html</u>

# Appendix E. Summary and Land Use Statistical Results

## **Summary Statistics**

Kaplan-Meier non-parametric statistics were employed to calculate summary statistics: mean, median, standard error, and lower and upper confidence levels. Summary statistics were produced only for parameters where data sets contained a minimum of a 50% detection rate, categorized as Case A in this report.

Parameters were categorized as Case B if the data set contained greater than a 50% rate of nondetects, or as Case C for data sets with greater than 80% non-detects. Due to the interim nature of this report, summary statistics were not produced for Case B or C parameters. The range of both detected concentrations and of reporting limits for non-detected concentrations are reported for Case B and C parameters.

## Land Use Statistic

A simple statistic that effectively compares the distribution of the range of data (the edf plots) by land use is employed here as an indicator of a land use effect on the stormwater concentrations. Helsel (2012) reports that the Peto-Prentice version of generalized Wilcoxon score test has the best overall performance given data of unequal sample sizes and unequal censoring between groups. The Peto-Prentice test identifies when at least one land use among the four has significantly different concentrations. Parameters are highlighted in purple shading (Tables E-1 – E-3) to indicate parameters with land use significance (Peto-Prentice p-value <0.05).

For this interim report, pair-wise comparisons were not conducted so the land use(s) with significant differences are not known. These comparisons will be done for the final report. However, the statistical plots in Appendix D give indications of which land uses have the lowest and highest ranges of detected concentrations.

				Kaplan-Meier (KM) Summary Statistics Peto-Pres				o-Prentice				
Parameter	Case	No. of Samples	% Censored	Mean	Mean Std Error	Mean 95 LCL	Mean 95 UCL	Median	Std Dev	p Value	Chi Sq	DF
Conventionals												
Fecal Coliform water (cfu/100 mL)	А	275	9.1	2783	660	1490	4077	400	10943	3.1E-12	56.6	3
Conductivity water (uS/cm)	А	373	0	129.7	15.6	99.1	160.2	85.0	300.9	1.2E-46	216.4	3
Hardness as CaCO <sub>3</sub> water (mg/L)	А	373	0	39.5	4.1	31.4	47.6	29.0	79.8	1.7E-27	127.7	3
Turbidity water (NTU)	А	284	0	27.2	1.8	23.6	30.8	18.0	31.0	3.1E-08	37.8	3
Total Suspended Solids water (mg/L)	А	347	0.3	57.4	4.1	49.3	65.4	34.7	76.6	1.7E-10	48.4	3
pH water (s.u.)	А	166	0	6.9	0.0	6.9	7.0	7.0	0.5	1.7E-02	8.2	2
Chloride water (mg/L)	А	325	3.4	8.7	1.4	5.9	11.4	3.5	25.4	9.9E-25	114.8	3
Surfactants water (mg/L) Biochemical Oxygen Demand water	А	346	43.6	0.06	0.004	0.05	0.07	0.038	0.08	9.9E-15	68.3	3
(mg/L)	А	303	27.1	7.1	1.5	4.2	10.0	3.6	25.7	2.5E-15	71.1	3
Total Solids, sediment (%)	А	18	0	35.7	5.0	25.9	45.4	39.5	21.2	0.37	3.2	3
Total Organic Carbon, sediment (%)	А	15	0	16.2	4.0	8.5	24.0	11.0	15.3	0.65	1.7	3
Nutrients												
Ortho-phosphate water dissolved (mg/L)	А	300	10.7	0.033	0.002	0.029	0.037	0.022	0.034	4.3E-15	70.0	3
Nitrite-Nitrate water dissolved (mg/L)	А	337	0.6	0.6	0.0	0.5	0.7	0.3	0.7	6.0E-03	12.4	3
Total Kjeldahl Nitrogen water (mg/L)	А	328	6.1	1.3	0.1	1.1	1.5	0.9	2.0	1.2E-05	25.6	3
Total Phosphorus water (mg/L)	А	332	1.2	0.2	0.0	0.1	0.2	0.1	0.1	1.4E-03	15.6	3

 Table E-1. Summary statistics for Case A: conventional and nutrient parameters.

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section.

LCL: lower confidence level

UCL: upper confidence level

DF: degrees of freedom

					Kaplan-I	Meier (KM	) Summar	y Statistics		Pe	to-Prentice	
Parameter	Case	No. of Samples	% Censored	Mean	Mean Std Error	Mean 95 LCL	Mean 95 UCL	Median	Std Dev	p Value	Chi Sq	DF
Metals												
Cadmium solid/sediment (mg/Kg, dw)	А	15	13.3	0.8	0.2	0.4	1.2	0.7	0.7	0.09	6.5	3
Cadmium water (ug/L)	А	379	28	0.18	0.02	0.15	0.21	0.11	0.30	8.1E-34	157.0	3
Cadmium water dissolved (ug/L)	А	375	40.8	0.1	0.0	0.1	0.1	0.0	0.1	2.4E-35	164.1	3
Copper solid/sediment (mg/Kg, dw)	А	15	0	73.1	25.4	23.4	122.9	16.6	98.3	0.09	6.6	3
Copper water (ug/L)	А	374	1.3	16.2	0.9	14.4	18.0	10.2	17.9	2.6E-37	173.2	3
Copper water dissolved (ug/L)	А	343	2.3	6.1	0.4	5.3	6.9	4.0	7.4	2.7E-18	84.9	3
Lead solid/sediment (mg/Kg, dw)	А	15	13.3	74.8	28.9	18.1	131.5	5.9	112.1	0.37	3.1	3
Lead water (ug/L)	А	374	1.9	14.5	1.3	12.0	16.9	4.6	24.2	4.4E-35	162.9	3
Lead water dissolved (ug/L)	А	364	20.9	1.1	0.2	0.8	1.4	0.2	3.1	1.2E-21	100.5	3
Magnesium water (ug/L)	А	179	0	2822	563	1718	3925	1600	7534	3.0E-24	112.6	3
Mercury solid/sediment (mg/Kg, dw)	А	8	12.5	0.1	0.0	0.1	0.2	0.1	0.1	NA	NA	NA
Zinc solid/sediment (mg/Kg, dw)	А	15	0	318	90	142	493	146	347	3.4E-02	8.7	3
Zinc water (ug/L)	А	370	1.1	107.8	7.3	93.4	122.1	71.7	141.0	4.3E-29	135.1	3
Zinc water dissolved (ug/L)	А	356	1.7	58.9	6.0	47.2	70.7	29.8	113.2	2.4E-15	71.2	3
<i>Total Petroleum Hydrocarbon</i> Diesel Range Hydrocarbons water (ug/L) Heavy Oil Range Hydrocarbons water	А	307	26.7	428	35	360	497	220	612	5.1E-12	55.6	3
(ug/L)	А	116	9.5	710	115	483	936	270	1243	5.8E-16	74.1	3
Heavy Fuel Oil water (ug/L)	А	119	14.3	915	112	696	1135	480	1222	5.0E-17	75.1	2
Lube Oil water (ug/L)	А	27	14.8	1863	249	1376	2351	1400	1292	8.9E-03	9.5	2
Motor Oil water (ug/L)	А	44	13.6	1334	144	1052	1616	1000	955	0.33	2.2	2

#### Table E-2. Summary statistics for Case A: metals and TPH parameters.

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section.

LCL: Lower confidence level

UCL: Upper confidence level

DF: Degrees of freedom

#### Table E-3. Summary statistics for Case A: PAHs and other organic contaminants.

					Kaplan-	Meier (KM	() Summar	y Statistics		Pet	o-Prentice	e
Parameter	Case	No. of Samples	% Censored	Mean	Mean Std Error	Mean 95 LCL	Mean 95 UCL	Median	Std Dev	p Value	Chi Sq	DF
PAHs												
Anthracene solid/sediment (ug/Kg, dw)	А	15	33.3	433	271	neg	965	94	1051	0.13	5.7	3
Benz[a]anthracene solid/sediment (ug/Kg, dw)	А	7	0	3829	3363	neg	10420	580	8898	NA	NA	NA
Benzo(a)pyrene solid/sediment (ug/Kg, dw)	А	15	26.7	2576	2204	neg	6896	220	8538	0.08	6.8	3
Benzo(b)fluoranthene solid/sediment (ug/Kg, dw)	Α	12	25	3990	2943	neg	9758	240	10196	NA	NA	NA
Benzo(g,h,i)perylene solid/sediment (ug/Kg, dw)	А	7	0	4184	3638	neg	11314	540	9625	NA	NA	NA
Benzo(k)fluoranthene solid/sediment (ug/Kg, dw)	Α	12	33.3	3409	2692	neg	8685	198	9325	NA	NA	NA
Chrysene solid/sediment (ug/Kg, dw)	Α	15	6.7	3333	2490	neg	8214	809	9645	2.8E-02	9.1	3
Dibenz[a,h]anthracene solid/sediment (ug/Kg, dw)	Α	15	33.3	754	608	neg	1946	79	2356	0.08	6.8	3
Fluoranthene solid/sediment (ug/Kg, dw)	Α	15	6.7	6538	4615	neg	15583	1460	17874	3.6E-02	8.6	3
Fluoranthene water (ug/L)	Α	369	41.7	0.3	0.11	0.08	0.5	0.03	2.1	2.9E-37	173.0	3
Indeno(1,2,3-cd)pyrene solid/sediment (ug/Kg, dw)	Α	15	6.7	2852	1594	neg	5975	400	6172	0.08	6.9	3
Phenanthrene solid/sediment (ug/Kg, dw)	Α	15	13.3	2646	1917	neg	6404	455	7425	0.14	5.5	3
Pyrene solid/sediment (ug/Kg, dw)	Α	15	0	6232	4149	neg	14364	1300	16069	4.8E-02	7.9	3
Pyrene water (ug/L)	Α	369	37.1	0.3	0.1	0.1	0.5	0.0	1.7	2.1E-32	150.4	3
<i>Other Organics</i> Bis(2-ethylhexyl) phthalate solid/sediment (ug/Kg,												
dw)	Α	13	0	6164	1600	3029	9299	4400	5767	0.08	6.8	3
Bis(2-ethylhexyl) phthalate water (ug/L)	Α	368	31.2	1.7	0.1	1.5	2.0	0.9	2.4	5.9E-33	153.0	3
Butyl benzyl phthalate solid/sediment (ug/Kg, dw)	А	15	46.7	931	524	neg	1958	96	2029	NA	NA	NA
Phenol solid/sediment (ug/Kg, dw)	Α	10	40	206	69	70	341	160	218	NA	NA	NA
PCB-aroclor 1254 solid/sediment (ug/Kg, dw)	Α	8	37.5	86.6	24.4	38.8	134.5	41.0	69.0	NA	NA	NA
p-Cresol solid/sediment (ug/Kg, dw)	А	7	14.3	1415	968	neg	3312	170	2561	NA	NA	NA

Purple shading indicates the Case A parameters with land use significance (Peto-Prentice p-value <0.05) in this interim assessment. Land use significance test is discussed in the *Methods* section.

LCL: Lower confidence level

UCL: Upper confidence level

DF: Degrees of freedom

neg: A low value less than zero

# Appendix F. Glossary, Acronyms, and Abbreviations

## Glossary

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

**Conductivity:** A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

**Fecal coliform:** That portion of the coliform group of bacteria which is present in intestinal tracts and feces of warm-blooded animals as detected by the product of acid or gas from lactose in a suitable culture medium within 24 hours at 44.5 plus or minus 0.2 degrees Celsius. Fecal coliform are "indicator" organisms that suggest the possible presence of disease-causing organisms. Concentrations are measured in colony forming units per 100 milliliters of water (cfu/100 mL).

**National Pollutant Discharge Elimination System (NPDES):** National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

**Nutrient:** Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

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

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

**Percentile:** A statistical number obtained from a distribution of a data set.

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

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

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

**Turbidity:** A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

## Acronyms and Abbreviations

BEHP	bis(2-Ethylhexyl) phthalate
BMP	Best management practice
BOD	Biological oxygen demand
BTEX	Benzene, toluene, ethylbenzene, and xylene
Ecology	Washington State Department of Ecology
edf	Empirical Distribution Function
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GIS	Geographic Information System
KM	Kaplan-Meier
MDL	Method detection limit
MQO	Measurement quality objective
NSQD	National Stormwater Quality Database
NURP	National Urban Runoff Program
NWTPH	Northwest Total Petroleum Hydrocarbon
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
QA	Quality assurance
QC	Quality control
ROS	Regression on Order Statistics
SVOC	Semi-volatile organic compound
TIA	Total impervious area
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
WAC	Washington Administrative Code
WQP	Water Quality Program

Units of Measurement

°C	degrees centigrade
dw	dry weight
kg	kilograms, a unit of mass equal to 1,000 grams
mg	milligram
mg/Kg	milligrams per kilogram (parts per million)

mg/L	milligrams per liter (parts per million)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
s.u.	standard units
ug/Kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter
uS/cm	microsiemens per centimeter, a unit of conductivity