Lower Duwamish Waterway Source Control: Upper and Middle Green River Surface Water Data Report

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King County

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Acronyms

µg/L	micrograms per liter
ANOVA	analysis of variance
AXYS	AXYS Analytical Services, Ltd.
cfs	cubic feet per second
DOC	dissolved organic carbon
EPA	U.S. Environmental Protection Agency
FOD	frequency of detection
GC/MS	Gas Chromatography/Mass Spectrometry
HPAHs	high molecular weight polycyclic aromatic hydrocarbons
ICP-MS	inductively coupled plasma-mass spectrometry
KCEL	King County Environmental Laboratory
L	liter

LDW	Lower Duwamish Waterway
LMCL	lowest method calibration limits
LPAHs	low molecular weight polycyclic aromatic hydrocarbons
MDL	method detection limit
mg/L	milligrams per liter
NTR	National Toxics Rule
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
pg/L	picograms per liter
QC	quality control
R^2	coefficient of determination
RM	river mile
RDL	reporting detection limit
RPD	relative percent difference
SAP	sampling and analysis plan
SDL	specific detection limit
SOP	standard operating procedure
TOC	total organic carbon
TSS	total suspended solids
USGS	United States Geological Survey
WQS	water quality standard

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EXECUTIVE SUMMARY

King County is currently conducting several studies to characterize potential sources of contaminants of concern identified in the Lower Duwamish Waterway (LDW) Superfund site. These studies evaluate chemical concentrations in water, sediment and suspended solids in the Green River Watershed and in atmospheric deposition within the Green/Duwamish River Watershed that may contribute chemical inputs to the LDW.

This is one of those studies and it presents an assessment of water quality in the Upper and Middle Green River, both above and below the Howard Hanson Dam. This effort was designed to complement a previous study that evaluated water quality in more developed areas of the Green River. The purpose of this effort was to better understand the relative concentrations of contaminants of concern for the LDW in the upper and middle reaches of the Green River that are further removed from developed areas and contaminant sources. These contaminants of concern are key human health risk drivers and include arsenic, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The study was designed to address the following questions:

- How do the relative concentrations of arsenic, PAHs and PCBs differ between dry season/baseflow and wet season/storm conditions for the Upper and Middle Green River Basin sites?
- What are initial estimates of the relative concentrations of PCBs, PAHs and arsenic from the Upper Green River Basin to the Middle and Lower Green River?

This study included analysis of water samples collected from three locations. Two sites were located approximately 20 miles above the Howard Hanson Dam; one on the mainstem Green River (river mile 85) and a second on a major tributary, Sunday Creek (river mile 82). A third site was located below the Dam in the middle reach of the Green River at Kanaskat-Palmer State Park at river mile 56. At the Kanaskat-Palmer location, three composite samples were collected during the dry season to represent baseflow conditions, while seven composite samples were collected during storm events. At each of the two locations upstream of the Dam, three composite baseflow and three composite storm event samples were collected. Samples were analyzed for arsenic, PAHs, PCBs as congeners, total organic carbon (TOC), dissolved organic carbon (DOC) and total suspended solids (TSS). These data will be used to characterize water quality in the upper and middle reaches of the Green River to improve the understanding of these contaminants and inform future source control efforts in the watershed.

Statistical differences between baseflow and storm conditions were only observed for arsenic at Kanaskat-Palmer. The lack of differences between sites for other parameters could be due to low sample size or reduced contaminant input during storm conditions due to limited development in the drainage basins contributing to these locations. When sites above the Dam were compared to the site below the Dam, higher concentrations of arsenic were observed at the downstream site; Kanaskat-Palmer.

Key findings of this study are presented below:

- The equipment blank results indicated that environmental samples collected with autosamplers were contaminated with PCBs and thus the results were biased high. A subsequent study determined the type of silicone tubing used with the autosampler and sample splitting process was the source of the PCB contamination (i.e., congeners PCB-47, PCB-51, and PCB-68). Based on this, the PCB totals presented in this study were adjusted to exclude the PCB congeners associated with silicone tubing used in sample collection and processing.
- At Kanaskat-Palmer, total and dissolved arsenic concentrations were statistically different between baseflow and storm event conditions, with higher concentrations observed during baseflow. At all three sampling locations, no other parameters (e.g., PCBs) with greater than 75% frequency of detection were statistically different between flow conditions.
- During storm events, total and dissolved arsenic were statistically different at the sampling locations (above and below the Dam), with higher concentrations observed at Kanaskat-Palmer. DOC concentrations during storm events were statistically different between the sites, but higher concentrations were detected at the Upper Green Basin sites. PCB concentrations were not statistically different between locations.
- Storm event results at the Upper Green Basin sites and Kanaskat-Palmer were statistically compared to results from the previous sampling efforts further downstream on the Green River; i.e., Flaming Geyser State Park (river mile 41) and Foster Links Golf Course (river mile 10). During storm events, average concentrations of TSS, arsenic, total high molecular weight PAHs, and total PCBs generally increased from upstream to downstream. Statistical differences in storm event concentrations between sites were observed for TSS and arsenic. For most parameters, the increases were less pronounced during baseflow conditions, although statistical differences were not tested due to low sample size. These findings suggest that stormwater runoff from more developed downstream areas may be contributing to increasing contaminant concentrations in the lower reaches of the Green river.
- Dissolved arsenic and total PCB concentrations were well below Washington State water quality standards for the protection of aquatic life. Individual PAH and total PCB concentrations were below NTR criteria for human health, but total PCB concentrations at all sites were above the new Washington State human health water quality standards (as of 2016).

1.0. INTRODUCTION

In 2018, King County completed a study that confirmed using standard silicone tubing in sample collection and processing of surface water samples results in a consistent, high bias to total PCB concentrations (King County 2018). This report has been revised to reflect these findings. The PCB totals in this revised version exclude the PCB congeners (i.e., PCB-47, PCB-51, and PCB-68) associated with the silicone tubing used in sampling. The results and conclusions for PCBs in previous versions of this report are superseded by this revised report. Please see the PCB Equipment Blank Study (King County 2018) for more details.

This report presents an assessment of water quality in the Upper and Middle reaches of the Green River to better understand the relative contribution of contaminants of concern to the Lower Duwamish Waterway (LDW)[1] from upstream areas in the Green River. These contaminants of concern are key human health risk drivers and include: polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and arsenic.

In 2011 and 2012, King County conducted an assessment of water quality in the Green River Watershed that included six sampling locations; two sites on the mainstem Green River and sites on four major tributaries to the Green River (King County 2014a). As part of that effort, recommendations were made to evaluate water quality further upstream on the Green River, both above and below the Howard Hanson Dam. This study addresses those recommendations and includes sampling locations that are further removed from developed areas. These sampling sites were selected to better understand factors in the less developed areas of the watershed that may be contributing contaminants to surface waters. This report presents these data and compares them to the 2011/2012 data collected from the mainstem of the Green River. The additional sampling was designed to supplement one of the original study questions (King County 2014a):

- How do the relative contributions of PCBs, PAHs, and arsenic differ during dry season baseflow and wet season/storm conditions?

Two additional study questions were developed for the Upper Green River Basin sampling efforts:

- What are the concentrations of PCBs, PAHs, and arsenic during dry season baseflow and wet season storm event conditions in the Upper Green River Basin where contaminant sources are very limited?
- What are initial estimates of the relative contributions of PCBs, PAHs, and arsenic from the Upper Green River Basin to the Middle and Lower Green River?

This study includes analysis of surface water samples collected from three locations including two locations upstream of the Dam and one location downstream of the Dam on the Green River. This data report presents and discusses the results of the 2013 sampling

[1] The LDW is about 5 miles long and consists of the downstream portion of the Duwamish River, excluding the East and West Waterways.

program (King County 2013a; b) with respect to the three study questions presented above.

This report is organized as follows: study background and geographic study area (Section 1.0); sample collection and processing methods (Section 2.0); laboratory analytical methods (Section 3.0); data analysis procedures (Section 4.0); study results (Section 5.0); and discussion (Section 6.0) and conclusions and key findings (Section 7.0). Supporting appendices include chain of custody forms, laboratory data results, and chemistry data validation reports.

1.1 Study Background

King County is a member of the Source Control Work Group for the LDW Superfund site. Other members include Washington State Department of Ecology (lead agency), the U.S. Environmental Protection Agency (EPA), City of Seattle, and the Port of Seattle. The Source Control Work Group collaborates to understand potential sources of contaminants to the LDW Superfund site and works to control and reduce sources that can contaminate sediments and resident fish and shellfish in the waterway. King County wants to better understand potential sources and pathways of the contaminants of concern identified in the LDW Superfund site that may contribute chemical inputs to the LDW. The County is currently conducting several studies to evaluate chemical concentrations in various media (e.g., air, water, sediments) in the Green/Duwamish Watershed.

King County previously completed chemical analysis of whole water samples at a number of combined sewer overflows in the LDW Basin (King County 2011a) and has been characterizing solids within the combined sewer structures and lines that discharge to the LDW (King County 2011b). King County recently completed sediment and water quality studies in the Green River Watershed (King County 2014a; b), and is currently conducting a study to evaluate chemical concentrations in suspended solids in the Green River Watershed (King County 2013c). The County has also been measuring chemical mass flux in atmospheric deposition within the Green/Duwamish River Watershed (King County 2011d; 2013d; e). The water quality study presented here is intended to complement data from these additional studies, as well as characterize the water quality in less developed areas of the Green River for select parameters.

The LDW Remedial Investigation (Windward 2010) indicates that more than 99% of the new sediment deposited in the LDW each year originates upstream of the LDW in the Green/Duwamish River. As a result, future LDW surface sediment quality will be closely tied to the quality of incoming sediment from the Green/Duwamish River. Previous assessments have been conducted to evaluate chemical concentrations in surface water and suspended solids in the Green/Duwamish River system (Herrera 2005; Herrera 2007; Gries and Sloan 2009; Windward 2010). The Green River Water Quality Assessment evaluated conventional parameters, nutrients, bacteria, metals, and organic compounds in the Green/Duwamish River (Herrera 2005). However, most organic compounds were infrequently or never detected. In particular, PAHs had low detection frequency and PCBs (as Aroclors®) were not detected, in part due to analytical methods and associated method detection limits. While arsenic concentrations in the Green River mainstem and associated tributaries were characterized in this 2005 study, no samples were collected from above Dam.

The primary purpose of this sampling and analysis effort is to improve the understanding of contaminant concentrations in the Upper and Middle reaches of the Green River. King County is interested in measuring concentrations of key contaminants in areas of the watershed where chemical sources are limited. There is also an interest to better understand the potential for migrating salmon to serve as a possible PCB source. To begin to address these questions, surface water samples from the Upper Green River Basin, above the Dam, where access by anadromous salmon is restricted and contaminant sources are limited, were collected and analyzed. Water samples were also collected from the Green River at Kanaskat-Palmer State Park below the Dam. This location is accessible to anadromous salmon. While contaminant sources are relatively limited in these areas, some potential sources include atmospheric deposition (PCBs and PAHs), local geology (arsenic), as well as the BNSF rail line crossing the drainage basin of Sunday Creek (PAHs from creosote treated rail timbers and diesel exhaust), and potentially from structures/building materials associated with the Dam and water diversion structures (PCBs).

These data will be used to characterize water quality in the upper reaches of the Green River and inform future source control efforts in the watershed. Combined with data from the previous downstream evaluation, these data will provide a better understanding of the location and magnitude of various contaminant inputs and their ultimate impact on the LDW.

This study focuses on arsenic, PAHs, and PCBs because the LDW Remedial Investigation identified these chemicals as contaminants of concern for human health within the LDW and residual risks from resident seafood consumption are predicted to be present following cleanup. Dioxins/furans were also identified as contaminants of concern for human health; however, these compounds were not included in this study as they are not expected to be present at detectable levels in surface waters based on previous unpublished sampling results downstream in the Green/Duwamish River.

1.2 Study Area

The Green-Duwamish Watershed includes approximately 484 square miles of varied terrain and land uses ranging from forested headwater areas at the crest of the Cascade Mountains to the industrial and port facilities of the LDW and East and West Waterways. The study area specific to this report includes the upper portion of the Middle Green River and the Upper Green River. The study area extends from the Green River at Kanaskat-Palmer State Park (river mile [RM] 56) to approximately 20 miles upstream of the Dam along the Upper Green River (RM 85) including one major tributary, Sunday Creek (RM 82). The drainage area for each sampling location is shown in Table 1.

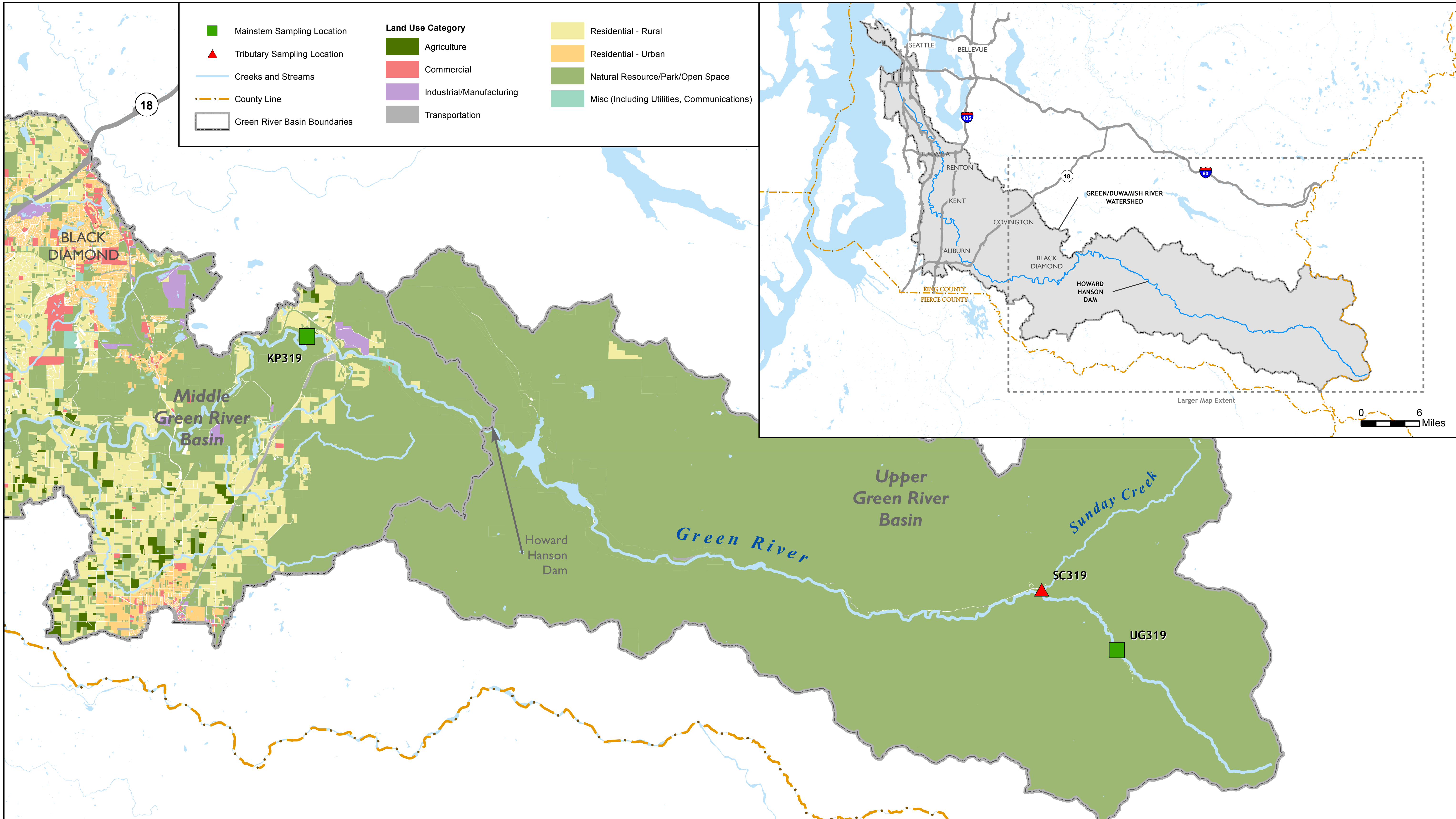
Table 1. Green River and tributary basin acreages for each sampling location

Site	Acreage
Mainstem Sites	
Upper Green River – RM 85	18,107
Green River – Kanaskat-Palmer – RM 52	153,526[a]
Tributary Basin	
Sunday Creek – at RM 82	15,553

[a] Includes all upstream basins
RM - river mile

Land use above and near the Green River at Kanaskat-Palmer State Park consists of more than 98% natural resource/open space, with 1% residential land use, and less than 1% other land use (commercial, transportation, manufacturing/industrial) (Figure 1). This location has slightly less development than the previous Middle Green River sampling location at Flaming Geyser State Park, which had almost 3% residential land use (King County 2014a). Land use above the two Upper Green River Basin locations is 100% natural resource land with only an access road as well as a rail line near Sunday Creek.

The three sampling locations are shown below in Figure 1.



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Shaun O'Neil 20130919

**Land use categories were designated based on King County Assessor data from May, 2013. Residential land was split into urban and rural based on the Urban Growth Area Line for 2013. Parcels with over 50% cultivated land cover, based on the 2007 Landsat Landcover classification, were designated as agricultural land.*

2 1 0 2
Miles
September 2013

N

Figure 1
Sampling Locations And Land Use In The Middle and Upper Green River Basins

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2.0. FIELD SAMPLING METHODS

The following section provides an overview of the field sampling methods used in this study. The details of the field procedures used for the study is described under two sampling and analysis plans (SAPs) and one SAP addendum. The sampling methods for the Kanaskat-Palmer location are described in the Green River Loading –Sampling and Analysis Plan (King County 2011c) and associated SAP Addendum (King County 2013a) and for the two Upper Green River Basin locations, sampling methods are described in Upper Green River Basin Water Quality Survey – Sampling and Analysis Plan (King County 2013b). Section 2.1 describes the sampling locations, while Section 2.2 summaries the field collection and sample processing methods. Section 2.3 summarizes the flow data collection methods, Section 2.4 describes the sampling events, and finally, Section 2.5 describes deviations from the SAPs related to field sampling methods. Copies of completed chain of custody forms used to track sample custody are included in Appendix A.

2.1 Sample Locations

Three locations were sampled, two above the Howard Hanson Dam and one location approximately 8.25 miles downstream from the Dam. The corresponding locator numbers and sample coordinates are shown in Table 2.

Table 2. Green River and tributary sampling locations and locator names

Locator	Report Nomenclature[a]	Locator Description	Northing[b]	Easting[b]
UG319	**Upper Green**	**Upper Green River –** approximately 20 miles upstream of the reservoir	70688	1499087
SC319	**Sunday Creek**	**Sunday Creek** – at 5200 Road bridge	79947	1487535
KP319	**Kanaskat-Palmer**	**Green River at Kanaskat-Palmer State Park** – west of day use shelters	119148	1373725

[a] Nomenclature used for each sampling location in tables and figures in this report
[b] State plane coordinates in North American Datum 1983 (NAD83) Washington State Plane North (4601)

2.2 Sample Collection and Processing

All samples were collected by King County Environmental Laboratory's Field Sciences Unit. Sample collection methods differed for the Green River at Kanaskat-Palmer and the two Upper Green River Basin locations. The methods are summarized below.

At the Kanaskat-Palmer location, 24-hour time-weighted composite surface water samples were collected using ISCO® autosamplers equipped with 10-liter glass carboys. Silicon tubing was used for the peristaltic pump, while Teflon® tubing was used as the intake lin. Teflon and silicon tubing was dedicated to the sampling location. Because of access challenges and associated logistical constraints, it was not feasible to collect time- or flow-weighted composite samples with an autosampler at the two Upper Green River Basin locations. Therefore, grab-composite samples were collected at these sites; 2-liter grab samples were collected approximately every 20 minutes over a two-hour period (total of 7 grabs and 14 liters per composite). Grab samples were placed into a 19-liter glass carboy once collected; the carboy was maintained on ice during the collection process.

All carboys were transported on ice to the King County Environmental Laboratory (KCEL). The composite samples were then homogenized and transferred into the appropriate laboratory sample containers. This was done by continuously agitating the sample in the carboy while transferring sample aliquots to the appropriate laboratory containers using a Teflon siphon tube and silicon tubing equipped peristaltic pump. Samples were analyzed for total and dissolved arsenic, PAHs, PCB congeners, total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS). Dissolved arsenic samples were filtered during the sample splitting process using a peristaltic pump. Because the dissolved arsenic sample aliquot could not be filtered within 15 minutes of collection, KCEL applied the appropriate hold-time violation flags to the data. Samples for PCB congener analysis were shipped to AXYS Analytical Services, Ltd. (AXYS) via overnight delivery within 1 to 4 months of sample collection. Samples were held at the KCEL at the appropriate temperature (4°C) until the shipment date.

At all three locations, the antecedent dry weather period was at least three days prior to collection of baseflow samples. Wet season storm event sample collection was triggered by a predicted rain event of at least 0.25 inches. After each storm event, the rain gage 40U, maintained by King County, was used to estimate precipitation in the vicinity of the Kanaskat-Palmer sampling location. The NOAA weather station at Lester, WA was used to estimate precipitation for the Upper Green River Basin sampling locations. Precipitation data associated with storm sampling events are presented in Section 5.7.

One ISCO autosampler equipment blank was collected at the KCEL on April 23, 2013. The equipment blank is used to evaluate contaminant levels that might be associated with the sampling equipment and introduce bias into the sample result. An aliquot of clean reverse osmosis water was processed through the ISCO autosampler equipment and analyzed for total and dissolved arsenic, PAHs, PCBs, TOC, DOC, and TSS. Because the equipment blank only represents the potential influence from the autosampler, not grab sample equipment, results for the equipment blank are only applicable to data collected at Kanaskat-Palmer for this study.

2.3 Flow Data Collection

Green River flow at the Kanaskat-Palmer location was estimated based on the United States Geological Survey (USGS) gage below the Dam (Gage 12105900). Flow was manually measured using a Swoffer flow meter (taken over a cross-section at each sampling location) during all but one sampling event at the Sunday Creek and Upper Green locations. During one storm event (November 19, 2013), stream conditions were unsafe to measure flow across the entire stream width, and therefore, no measurements were conducted.

2.4 Sampling Events

Sampling at the Kanaskat-Palmer location began in April, 2013. A total of 7 storm event samples were collected; three in April 2013, two in November 2013 and two in January 2014. Three dry season baseflow samples were collected at this location in July and September 2013.

At the Sunday Creek and Upper Green locations, baseflow samples were collected in September and October of 2013, while storm event samples were collected in October and November of 2013.

Table 3 lists the collection date, sample identification number and the flow condition for all samples collected at each location. Throughout the course of the sampling period, four field replicate samples were collected. One field replicate was collected at Kanaskat-Palmer, two at the Upper Green and one at Sunday Creek.

Table 3. Kanaskat-Palmer, Upper Green River and Sunday Creek tributary collection times, sample IDs and flow types

Site	Flow Condition	Sample Start Date-Time	Sample End Date-Time	Sample ID	Replicate
Equip Blank	Not Applicable	4/23/2013 11:25	4/23/2013 11:25	L57794-1	
Upper Green	Baseflow	9/4/2013 12:10	9/4/2013 14:10	L58657-2	
		9/10/2013 13:07	9/10/2013 15:07	L58688-2	
		9/10/2013 13:07	9/10/2013 15:07	L58688-3	Replicate
		10/17/2013 10:10	10/17/2013 12:10	L58976-1	
	Storm	10/1/2013 12:00	10/1/2013 14:00	L58861-1	
		10/1/2013 12:00	10/1/2013 14:00	L58861-3	Replicate
		11/7/2013 10:25	11/7/2013 12:25	L59148-1	
		11/19/2013 11:30	11/19/2013 13:30	L59240-1	
Sunday Creek	Baseflow	9/4/2013 11:56	9/4/2013 13:56	L58657-1	
		9/10/2013 13:02	9/10/2013 15:02	L58688-1	
		10/17/2013 9:55	10/17/2013 11:55	L58976-2	
	Storm	10/1/2013 11:50	10/1/2013 13:50	L58861-2	
		11/7/2013 10:30	11/7/2013 12:30	L59148-2	
		11/7/2013 10:30	11/7/2013 12:30	L59148-3	Replicate
		11/19/2013 11:20	11/19/2013 13:20	L59240-2	
Kanaskat-Palmer	Baseflow	7/10/2013 5:00	7/11/2013 5:00	L58246-1	
		9/10/2013 10:35	9/11/2013 10:35	L58708-1	
		9/19/2013 10:52	9/20/2013 10:52	L58791-1	
	Storm	4/4/2013 12:00	4/5/2013 11:30	L57715-1	
		4/10/2013 5:00	4/11/2013 4:30	L57751-1	
		4/18/2013 15:00	4/19/2013 14:30	L57772-1	
		11/6/2013 22:00	11/7/2013 21:30	L59149-1	
		11/18/2013 12:04	11/19/2013 12:04	L59239-1	

Site	Flow Condition	Sample Start Date-Time	Sample End Date-Time	Sample ID	Replicate
		1/8/2014 10:00	1/9/2014 9:30	L59470-1	
		1/8/2014 10:00	1/9/2014 9:30	L59470-2	Replicate
		1/29/2014 1:00	1/30/2014 0:30	L59595-1	

2.5 Deviations from the SAP

The Upper Green River SAP specified that baseflow samples were to be collected between July and September. Due to logistical difficulties, one baseflow sample at the Upper Green and Sunday Creek locations were collected in October 2013, after several heavy rain events. Because of this and because there was at least a three-day antecedent dry weather period before collection, these samples were considered wet-season baseflow conditions.

The Upper Green SAP specified that two replicates (one for each flow condition) would be collected at both the Upper Green and Sunday Creek locations; however, only one replicate was collected at the Sunday Creek location. The absence of one replicate will not adversely impact project objectives, although it does limit potential understanding of natural variability at the site, which can be significant at low concentrations at or below analytical method reporting limits.

The SAP addendum specified that PCB congeners would be analyzed in six storm event samples from Kanaskat-Palmer. However, only five samples were analyzed for PCB congeners. It was necessary to reanalyze a subset of samples due to method blank contamination that exceeded the method standard operating procedures. Back-up samples for two samples were compromised because the jars or lids were broken during shipment. Therefore, the laboratory could not re-analyze these samples. Only one storm sampling event was added to replace one of the two lost PCB samples.

The Upper Green SAP specified that a field blank would be collected for the grab-composited samples. No field blanks were collected for the grab-composite method described in the Upper Green SAP. This deviation limits the ability to evaluate equipment impacts on the grab-composite sample results.

The Upper Green SAP specified a three-day antecedent dry period for collection of baseflow samples. For the sample collected at Sunday Creek on September 4, 2013, some rainfall was recorded in the preceding 24 hours (0.04 inches); however, this is not expected to influence the overall utility of these data.

The SAP addendum specified that 24-hour composites were to be collected at the Kanaskat-Palmer location. Several storm event composites were collected just under this time specification (approximately 23.5 hours). This is not expected to influence the overall utility and comparability of these data.

3.0. LABORATORY METHODS

A summary of the laboratory analyses performed on all samples is presented in this section. Laboratory analyses were conducted by KCEL except PCB congeners, which were analyzed by AXYS Analytical Services, Ltd.

The KCEL reports both the reporting detection limit (RDL) and the method detection limit (MDL) for each sample and parameter, where applicable. For PCB congeners a high resolution isotopic dilution based method is used where the MDL and RDL terms are less applicable because limits of quantitation are derived from calibration capabilities and ubiquitous, but typically low level equipment and laboratory blank contamination. Thus, PCB congener data are reported to lowest method calibration limits (LMCL) and flagged as estimated down to the sample specific detection limit (SDL) value. The following sections provide a summary of the laboratory methods; greater detail can be found in the project SAPs (King County 2011c; 2013a;b).

3.1 Conventional Water Quality Parameters

All conventional analyses followed Standard Methods protocols (American Public Health Association [APHA] 1998). TOC and DOC were analyzed following Standard Methods 5310-B and TSS following Standard Methods 2540-D.

3.2 Arsenic

Total and dissolved arsenic samples were analyzed by EPA Method 200.8 (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL Standard Operating Procedure (SOP) 624. Total and dissolved arsenic samples were preserved to a pH less than 2 with ultrapure nitric acid for ICP-MS analysis once these aliquots were transferred to their sample containers from the composite carboy.

3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Samples were prepared by liquid-liquid extraction as detailed in EPA Method 3520C, KCEL SOP 701. Samples were analyzed according to EPA Method 8270D; Gas Chromatography/ Mass Spectrometry with Selected Ion Monitoring and Large Volume Injection method (GC/MS-SIM LVI). A draft SOP has been developed for this method but not yet finalized (SOP 772v0, draft). The specific PAHs analyzed included: 2-methylnaphthalene, acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, benzo(b,j,k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluorene, fluoranthene, indeno (1,2,3-cd)perylene, naphthalene, phenanthrene, and pyrene.

3.4 PCB Congeners

Samples were analyzed for all 209 PCB congeners. PCB congener analysis followed EPA Method 1668A Revision C (EPA 2010a), which is a high-resolution gas chromatography/ high-resolution mass spectroscopy method using an isotope dilution internal standard quantification. This method provides reliable analyte identification and very low detection limits. An extensive suite of labeled surrogate standards is added before samples are extracted. Data are "recovery-corrected" for losses in extraction and clean-up, and analytes are quantified against their labeled analogues.

AXYS performed this analysis according to their SOP MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668, which is a proprietary document. A one-liter sample was extracted followed by standard method clean-up, which includes layered Acid/Base Silica, Florisil and Alumina. Analysis was performed with an SPB Octyl column and a secondary DB1 column is used to resolve the co-eluting congeners PCB156 and PCB157. Method 1668C requires that if a sample contains more than 1% total solids, the solids and liquid will be extracted and analyzed separately; however none of these samples contained more than 1% solids.

3.5 Deviations from the SAP

There were no analytical method deviations from the SAP.

4.0. DATA ANALYSIS

The analytical data were prepared for data analysis by applying rules for determining PCB and PAH sums and use of laboratory and field replicate data. The details of these calculations, as well as a summary of data analysis methods, are described below.

4.1 Summation for PAHs and PCB Congeners

In addition to reporting the individual PAH results, the total high molecular weight PAHs (HPAHs) and total low molecular weight PAHs (LPAHs) are reported as the sum of detected HPAHs or LPAHs, respectively. If no PAHs were detected within the LPAH or HPAH class, the reported MDL for these totals is the highest MDL reported of the individual PAHs in that class. LPAHs were calculated as the sum of acenaphthene, acenaphthylene, anthracene, fluorene, naphthalene, and phenanthrene. HPAHs were calculated as the sum of benzo(a)anthracene, benzo(g,h,i)perylene, benzo(a)pyrene, benzo(b,j,k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-cd)perylene, and pyrene.

PCB data are presented as total PCB concentrations. When reporting total PCBs, only detected congeners are included in the total PCB sum. At least one PCB congener was detected in all samples.

4.2 Laboratory Duplicates and Field Replicates

Laboratory duplicates were considered laboratory quality control values and used during the data validation process to check method and analytical variability. Field replicate results were considered a second estimate of the sample and were combined with their primary sample result using the following rules:

- When sample results were non-detect (U-flagged) in both samples, the two U-flagged values were averaged. These were often the same MDL value.
- When one result was detected and one was a non-detect, the combined value was the average of the detected value and the non-detect value (U-flagged value). The resulting value was J-flagged (i.e., estimated) with an unknown bias.
- When both results were detected, the two concentrations were simply averaged. Any J-flags for either sample were carried over to the resulting average.

The total LPAHs, HPAHs, and PCBs were summed prior to applying these rules for field replicates.

Field replicates combine the analytical uncertainty with field and sampling heterogeneity. To describe this, the relative percent difference (RPD) between field replicates was calculated. RPD is the absolute difference between the replicates divided by the average and multiplied by 100. These results are presented in Section 5.5.2.

4.3 Statistical Analysis

Summary statistics (e.g., mean and median concentrations), were presented on a site-specific basis by baseflow or storm event conditions. These data summaries are presented in Section 5. Statistical analyses of the data are presented in Section 6.

All statistical analyses were conducted using Sigma Plot v12.5 software. Comparisons between two datasets were performed using two-tailed t-tests. This method was used to identify differences in concentration between baseflow and storm events at each location. Due to the small sample size, data for the two Upper Green River Basin locations were combined for this analysis. Two-tailed t-tests were also used to identify differences in storm event data between Kanaskat-Palmer and the combined Upper Green River Basin locations. If the data did not pass the Shapiro-Wilk Normality ($p<0.05$) or the Equal Variance ($p<0.05$) tests, then the non-parametric Mann-Whitney Rank Sum Test ($p<0.05$) was performed. Parametric tests evaluate differences based on the average, standard deviation, and sample size, whereas non-parametric tests are based on ranked values to determine if the medians are statistically different.

Data for previously collected and reported samples from the Green River at Flaming Geyser State Park (RM 41) and at Foster Links Golf Course (RM 10; in Tukwila)(King County 2014a) were included in an analysis with data collected at the three locations discussed in this report. These sites are herein referred to as Flaming Geyser and Foster Links, respectively. If the data did not pass the Shapiro-Wilk Normality test ($p<0.05$) or the Equal Variance test ($p<0.05$), the non-parametric Kruskal-Wallis one-way % (ANOVA) of ranks ($p<0.05$), followed by the Tukey test for pairwise multiple comparisons ($p<0.05$) was used. For parametric datasets, an ANOVA, followed by the Holm-Sidak method for pairwise multiple comparison ($p<0.05$) was used. Baseflow concentration data were not included in the comparison across all sites because of low sample size (most locations N = 3). Figures in Section 6 have significant differences labelled.

Relationships between select chemical and physical parameters were examined using linear regression analysis in Microsoft Excel 2010. A coefficient of determination (R^2) value greater than 0.5 suggests the y parameter (chemical) is moderately dependent on the x parameter (physical).

5.0. RESULTS

The following section provides a summary of the analytical results with sections 5.1 through 5.4 presenting conventional parameters, arsenic, PAH, and PCB data. All analytical data as reported by the laboratories are presented in Appendix B. A summary of the equipment blank data and a comparison of field replicate data are discussed in Section 5.5. A summary of data validation findings for all chemistry analyses is included in Section 5.6; complete data validation reports are included in Appendix C. Finally, flow and precipitation data are presented in Section 5.7.

5.1 Conventional Parameters

This section summarizes the TOC, DOC and, TSS results.

5.1.1 Total and Dissolved Organic Carbon

Total and dissolved organic carbon concentrations were detected in all samples (Table 4). In several samples, DOC detections exceeded TOC detections. While in theory this is not possible, it can occur due to sample heterogeneity, analytical variability (particularly with very low levels of organic carbon), or when most of the organic carbon is in the dissolved fraction. If differences between DOC and TOC were greater than expected analytical variability, then sample results were qualified by the laboratory as estimates (J-qualifier) (see Section 5.6.1).

Table 4. Summary of TOC and DOC (mg/L) data by site and flow condition

Site	Analyte	Flow	FOD	Min	Max	Average	Median
Upper Green	TOC	Base	3/3	0.75 J	3.29	1.95 J	1.81 J
		Storm	3/3	1.06	2.32	1.84	2.15
	DOC	Base	3/3	1.28 J	3.21	2.11 J	1.83 J
		Storm	3/3	1.23	2.16	1.84	2.12
Sunday Creek	TOC	Base	3/3	0.58 J	1.42 J	0.87 J	0.60 J
		Storm	3/3	1.12	1.82	1.54	1.68
	DOC	Base	3/3	0.94 J	2.59 J	1.52 J	1.03 J
		Storm	3/3	1.43	1.92	1.73	1.84
Kanaskat-Palmer	TOC	Base	3/3	1.30	1.58	1.45	1.48
		Storm	7/7	1.08	1.89	1.33	1.31
	DOC	Base	3/3	1.08	1.55	1.29	1.24
		Storm	7/7	0.86 J	1.71	1.15 J	1.09

FOD - frequency of detection; J estimated value

Total organic carbon concentrations during baseflow conditions ranged from 0.58 mg/L at Sunday Creek to 3.29 mg/L at the Upper Green location. During storm events, TOC ranged from 1.06 mg/L to 2.32 mg/L; both concentrations were detected at the Upper Green location. Figure 2 presents the individual concentration data for TOC. The range of TOC concentrations across site and flow condition was similar; however, TOC was most variable at the Upper Green location during baseflow conditions.

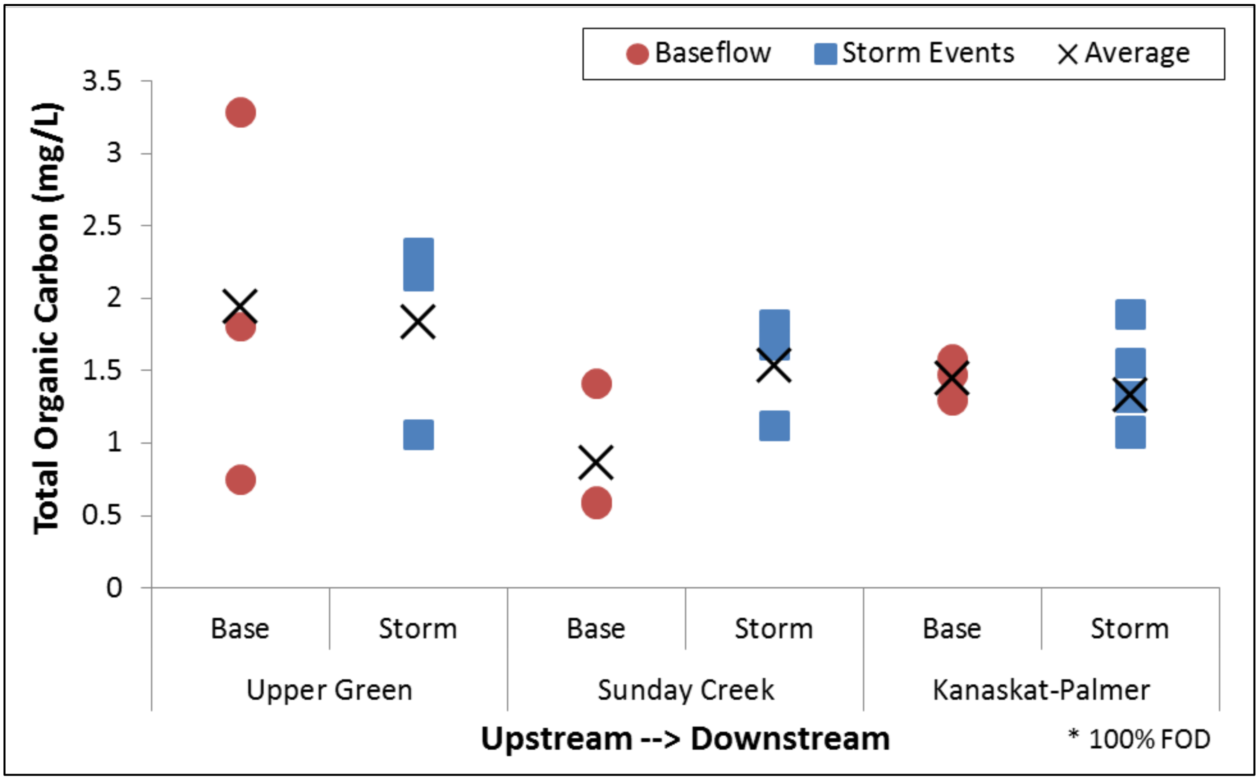

Figure 2. Total Organic Carbon by Site and Flow Condition

Dissolved organic carbon during baseflow conditions ranged from 0.94 mg/L at Sunday Creek to 3.21 mg/L at the Upper Green location. During storm events, DOC ranged from 0.86 mg/L at Kanaskat-Palmer to 2.16 mg/L at the Upper Green location. Figure 3 presents the individual data for DOC. The DOC concentrations overlap across site and flow conditions.

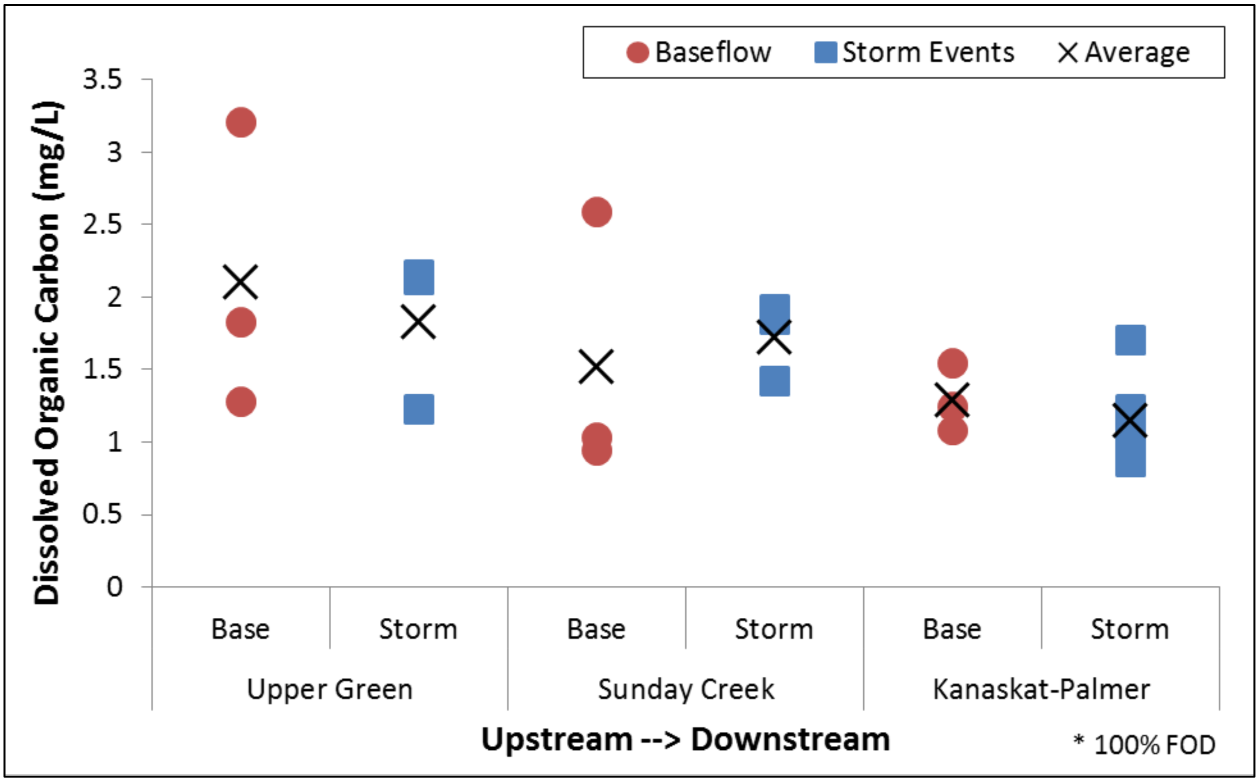

Figure 3. Dissolved Organic Carbon by Site and Flow Condition

5.1.2 Total Suspended Solids

Table 5 presents the summary statistics for TSS. Total suspended solids concentrations in all baseflow samples were below detection limits at Sunday Creek (MDL 0.5 or 1.0 mg/L) and the Upper Green location (MDL 1 mg/L). Detected concentrations at Kanaskat-Palmer during baseflow conditions ranged from 0.80 to 2.0 mg/L.

Table 5. Summary of TSS (mg/L) data by site and flow condition

Site	Flow	FOD	Min	Max	Average[a]	Median[a]
Upper Green	Base	0/3	n/d	n/d	0.58 U	–
	Storm	2/3	0.80 J	13.4	5.07 J	–
Sunday Creek	Base	0/3	n/d	n/d	0.83 U	–
	Storm	2/3	1.35	8.00	3.45 J	–
Kanaskat-Palmer	Base	3/3	0.80 J	2.0 J	1.5 J	1.8 J
	Storm	7/7	1.2 J	17.2	6.44 J	5.60

[a] Average and median concentrations were calculated with detected concentrations and the MDL for non-detect results. Medians were only calculated when there were more than 2 detections.
– not calculated; FOD frequency of detection; J estimated value; U non-detect; n/d non-detect

TSS was detected in all storm samples from the Green River at Kanaskat-Palmer. TSS was only detected during two of the three storm events at both Sunday Creek and the Upper Green location. The greatest variability in TSS was observed during storm conditions (Figure 4). Detected concentrations ranged from 0.8 mg/L at the Upper Green to 17.2 mg/L at Kanaskat-Palmer. The maximum TSS concentration at each site was observed during the same storm event (November 18-19, 2013).

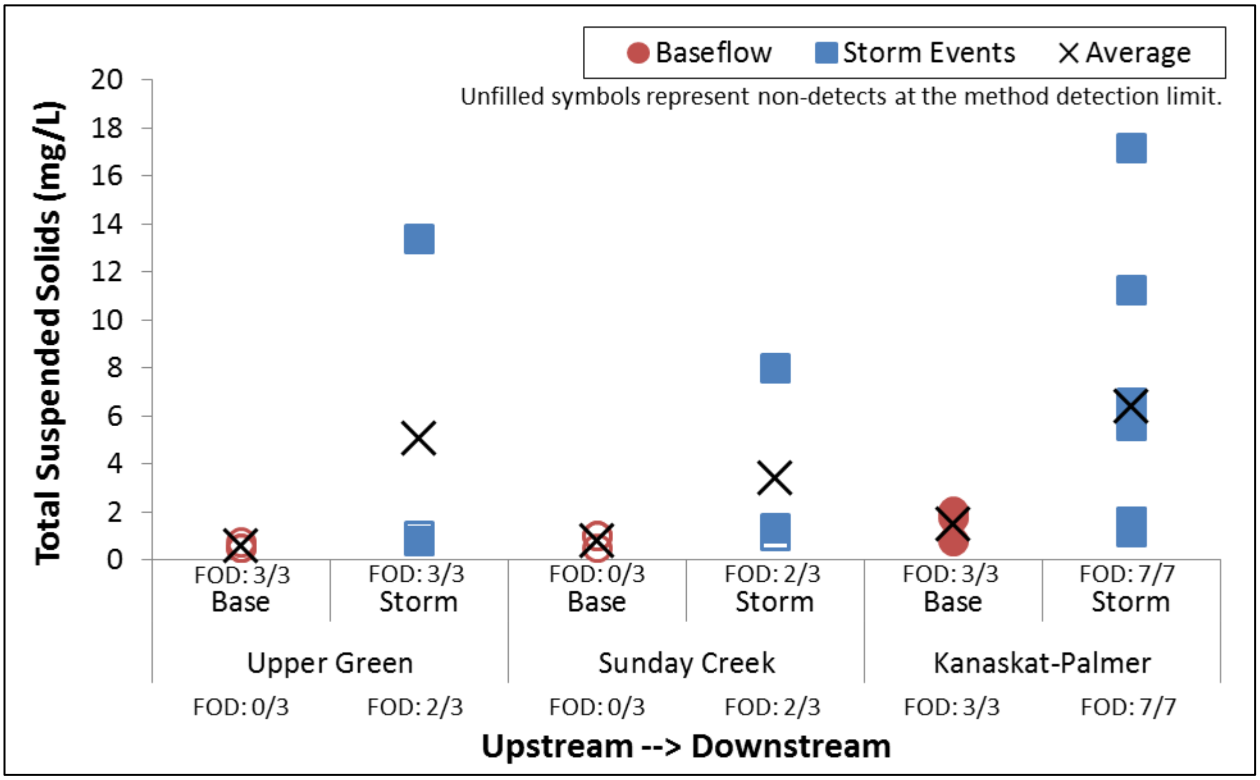

Figure 4. Total Suspended Solids by Site and Flow Condition

5.2 Total and Dissolved Arsenic

Arsenic was detected in all samples collected from Kanaskat-Palmer and the Upper Green, but was only detected in two of the three storm samples at Sunday Creek. Table 6 summarizes total and dissolved arsenic data by site and flow condition.

Table 6. Summary of total and dissolved arsenic (µg/L) data by site and flow condition

Site	Arsenic	Flow	FOD	Min		Max		Average[a]		Median[a]	
Upper Green	Total	Base	3/3	0.13	J	0.15	J	0.14	J	0.15	J
		Storm	3/3	0.16	J	0.20	J	0.18	J	0.17	J
	Dissolved	Base	3/3	0.12	J	0.16	J	0.14	J	0.15	J
		Storm	3/3	0.15	J	0.16	J	0.15	J	0.15	J
Sunday Creek	Total	Base	0/3	n/d		n/d		0.10	U	–	
		Storm	2/3	0.10	J	0.16	J	0.12	J	–	
	Dissolved	Base	0/3	n/d		n/d		0.10	U	–	
		Storm	1/3	n/d		0.11	J	0.10	J	–	
Kanaskat-Palmer	Total	Base	3/3	0.660		0.918		0.799		0.819	
		Storm	7/7	0.26	J	0.50	J	0.38	J	0.37	J
	Dissolved	Base	3/3	0.623	J	0.881	J	0.756	J	0.763	J
		Storm	7/7	0.23	J	0.39	J	0.30	J	0.29	J

[a] Average and median concentrations were calculated with detected concentrations and the MDL for non-detect results. Medians were only calculated with more than 2 detections.
–not calculated; FOD frequency of detection; J estimated value; U non-detect; n/d non-detect

During baseflow conditions, total arsenic concentrations ranged from non-detected at Sunday Creek to 0.918 µg/L at Kanaskat-Palmer. Total arsenic concentrations during storm events ranged from non-detected at Sunday Creek to 0.50 µg/L at Kanaskat-Palmer.

Dissolved arsenic concentrations followed a similar pattern, with non-detected or minimum detected arsenic concentrations observed at Sunday Creek and the Upper Green locations, respectively, during baseflow conditions. During storm events, dissolved arsenic was detected once in Sunday Creek (0.11 µg/L) and detected in all three Upper Green samples at relatively low concentrations of (0.15 to 0.16 µg/L). The maximum dissolved arsenic concentrations were observed at Kanaskat-Palmer ranging from 0.881 mg/L during baseflow conditions to 0.39 mg/L during storm events. The greatest variability in total and dissolved arsenic concentrations was observed at Kanaskat-Palmer (Figures 5 and 6). Total and dissolved concentrations during baseflow conditions were always higher than corresponding storm event concentrations at this location.

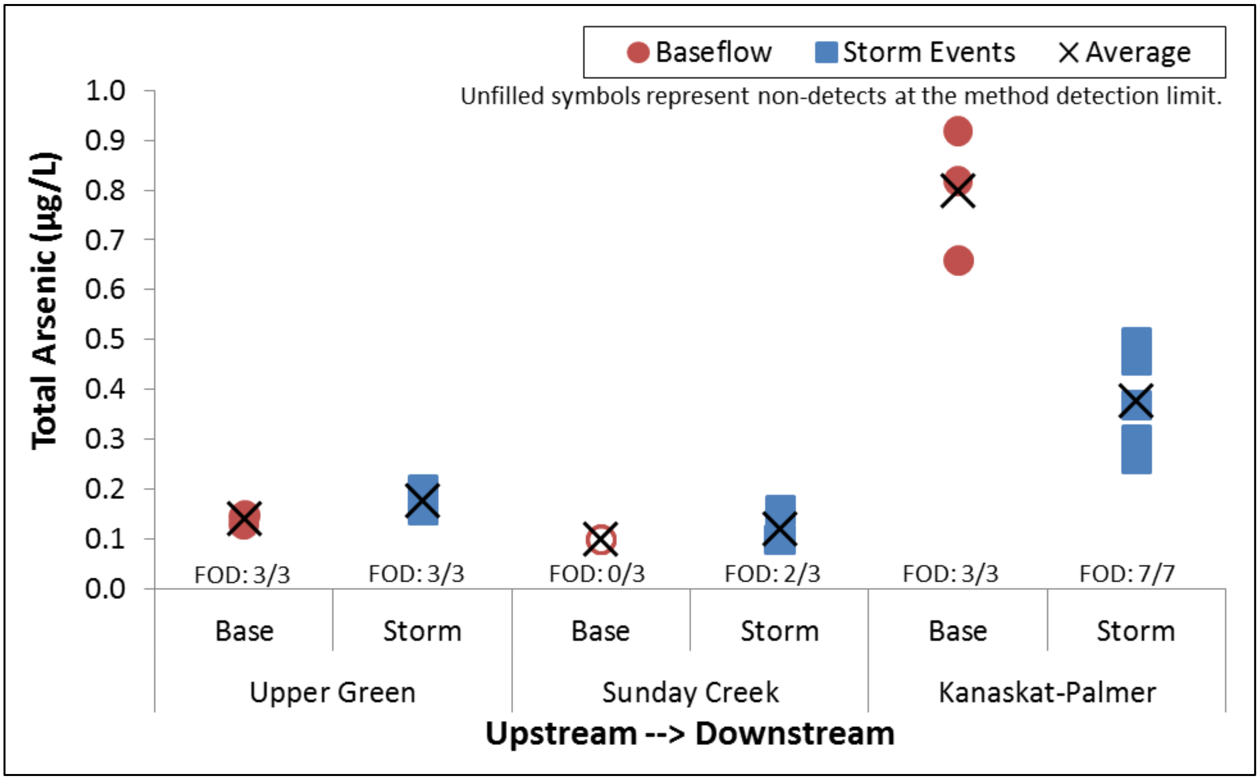

Figure 5. Total Arsenic by Site and Flow Condition

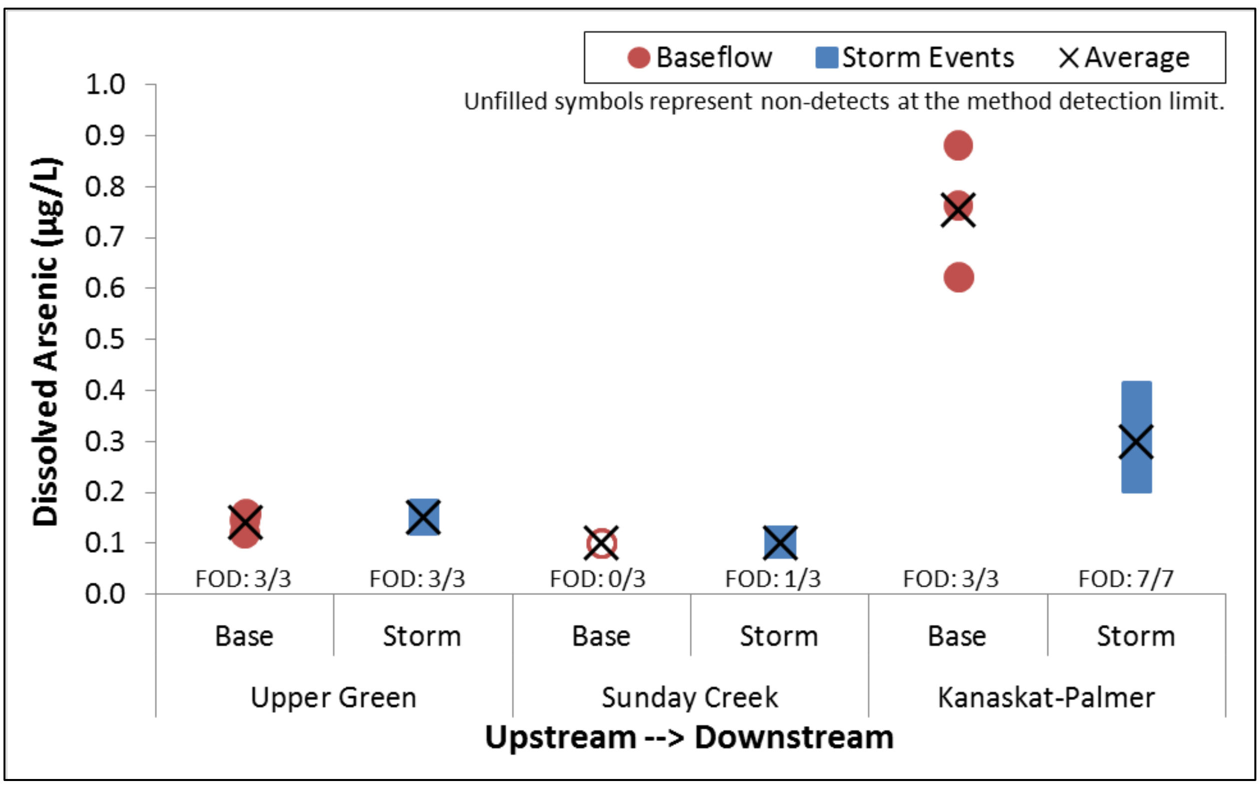

Figure 6. Dissolved Arsenic by Site and Flow Condition

5.3 Low and High Molecular Weight PAHs

Individual LPAH compounds were infrequently detected at Sunday Creek and the Upper Green locations; only two LPAHs, naphthalene and fluorine, were detected. At Kanaskat-Palmer, all LPAHs, except phenanthrene, were detected at least once. Naphthalene was the only LPAH detected in all samples at all sites. Table 7 summarizes the frequency of detection for individual LPAH compounds.

Table 7. Frequency of detection of PAH compounds by site and flow condition

Group	Compound	Kanaskat-Palmer		Sunday Creek		Upper Green	
		Base	Storm	Base	Storm	Base	Storm
LPAHs	Acenaphthene	2/3	5/7	0/3	0/3	0/3	0/3
	Acenaphthylene	1/3	1/7	0/3	0/3	0/3	0/3
	Anthracene	0/3	1/7	0/3	0/3	0/3	0/3
	Fluorene	0/3	5/7	1/3	1/3	1/3	3/3
	Naphthalene	3/3	7/7	3/3	3/3	3/3	3/3
	Phenanthrene	0/3	0/7	0/3	0/3	0/3	0/3
HPAHs	Benzo(a)-anthracene	0/3	2/7	0/3	0/3	0/3	0/3
	Benzo(a)pyrene	0/3	1/7	0/3	0/3	0/3	0/3
	Benzo(b,j,k)-fluoranthene	1/3	2/7	0/3	1/3	0/3	0/3
	Benzo(g,h,i)-perylene	0/3	1/7	0/3	0/3	0/3	0/3
	Chrysene	1/3	3/7	0/3	0/3	0/3	0/3
	Dibenzo(a,h)-anthrancene	0/3	1/7	0/3	0/3	0/3	0/3
	Fluoranthene	0/3	0/7	0/3	1/3	0/3	2/3
	Indeno(1,2,3-Cd)-pyrene	0/3	1/7	0/3	0/3	0/3	0/3
	Pyrene	0/3	0/7	0/3	0/3	0/3	0/3

Table 8 summarizes total LPAH concentrations by site and flow condition; individual data are presented in Figure 7. During baseflow conditions, total LPAH concentrations ranged from 0.0172 µg/L at Sunday Creek to 0.120 µg/L at the Upper Green location. Total LPAH concentrations during storm events ranged from 0.0196 µg/L at Kanaskat-Palmer to 0.133 µg/L at the Upper Green location. For most detected LPAH compounds, the concentration was qualified as estimated because it was below the RDL; the exception was naphthalene in which most detections were greater than the RDL (see Appendix B).

Table 8. Summary of Total LPAH and HPAH (µg/L) data by site and flow condition

Site	Sum	Flow	FOD	Min		Max		Average[a]		Median[a]	
Upper Green	LPAH	Base	3/3	0.0517		0.120		0.0831	J	0.0776	J
		Storm	3/3	0.0254	J	0.133	J	0.0727	J	0.0594	J
	HPAH	Base	0/3	n/d		n/d		0.000945	U	0.000943	U
		Storm	1/3	n/d		0.00030	J	0.000570	J	–	
Sunday Creek	LPAH	Base	3/3	0.0172	J	0.0960		0.0619	J	0.0724	
		Storm	3/3	0.0321		0.0809	J	0.0564	J	0.0562	
	HPAH	Base	0/3	n/d		n/d		0.00105	U	0.000943	U
		Storm	2/3	0.00030	J	0.00149		0.000911	J	–	
Kanaskat-Palmer	LPAH	Base	3/3	0.0205		0.0462	J	0.0294	J	0.0216	J
		Storm	7/7	0.0196	J	0.115	J	0.0410	J	0.0236	J
	HPAH	Base	1/3	n/d		0.00097	J	0.00095	J	–	
		Storm	3/7	0.000596	J	0.00653	J	0.00184	J	0.000943	U

[a] Average and median concentrations include non-detect results at the value of the highest detection limit of the compounds included in the sum (see Section 4.1). Medians were only calculated with more than 2 detections.
– not calculated; FOD frequency of detection; J estimated value; U non-detect; n/d non-detect

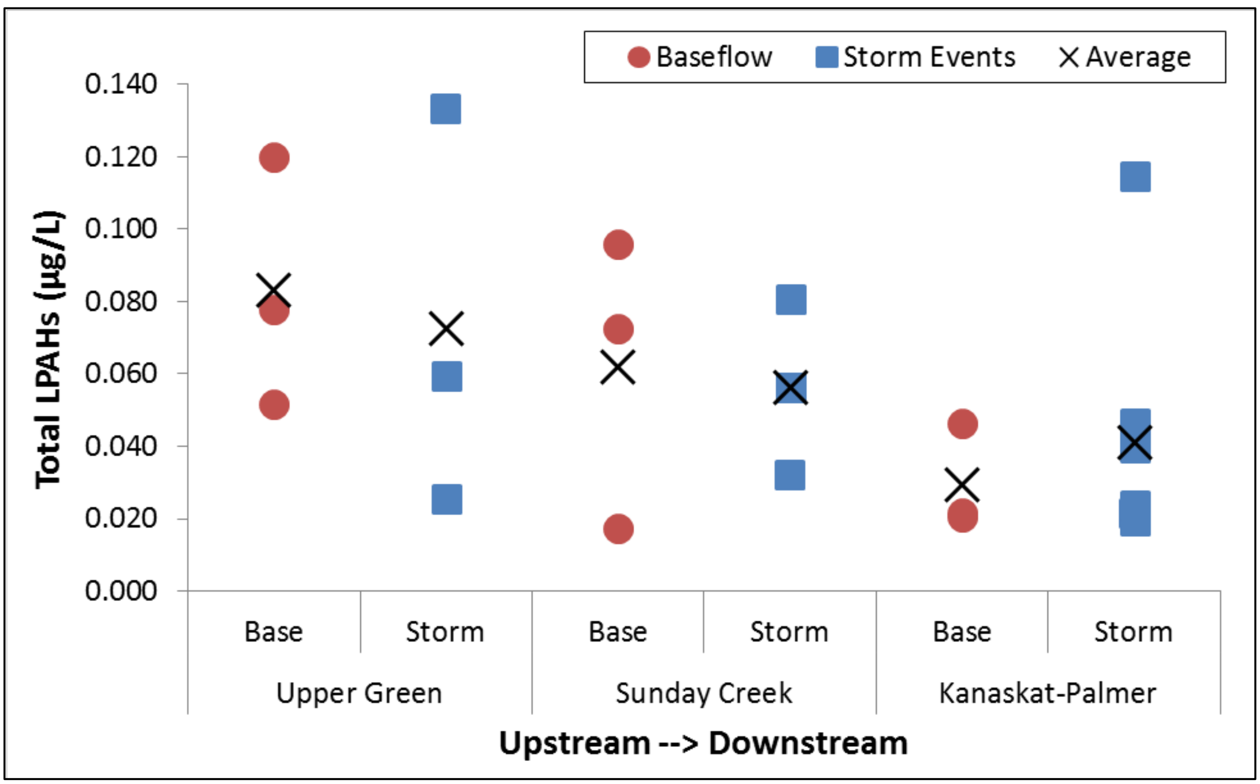

Figure 7. LPAHs by Site and Flow Condition

HPAH compounds were detected in only 7 of 22 samples (Table 7). Similar to the finding discussed above for LPAHs, HPAHs were infrequently detected at Sunday Creek and the Upper Green locations. When HPAHs were detected, typically only one to three HPAH compounds were found. The exception to this pattern was one storm sample from Kanaskat-Palmer (November 18-19, 2013) where seven compounds were detected.

Table 8 summarizes total HPAH concentrations by site and flow condition; individual data are presented in Figure 8. HPAHs were detected in just one baseflow sample from Kanaskat-Palmer (0.00097 µg/L). During storm events, HPAH concentrations ranged from a non-detect at the Upper Green to 0.00653 µg/L at Kanaskat-Palmer. For many of the detected HPAH compounds, the concentration was qualified as estimated because it was below the RDL (see Appendix B).

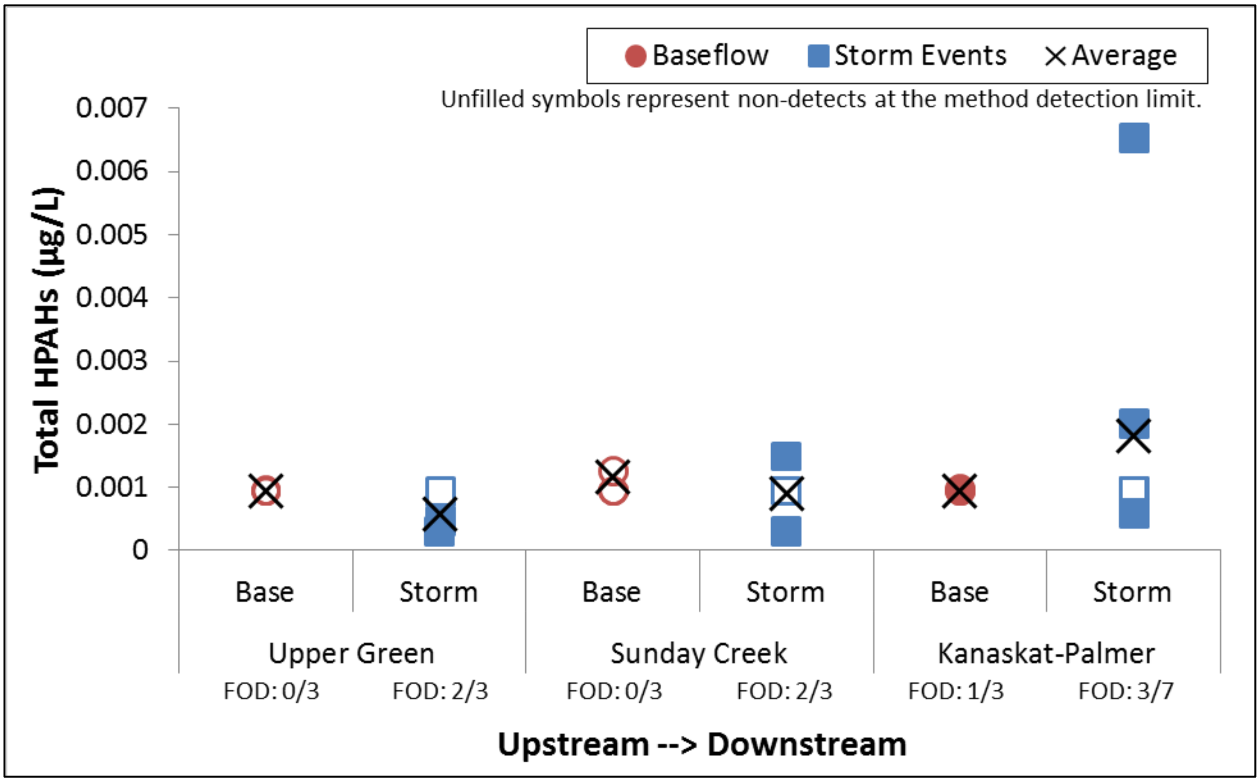

Figure 8. HPAHs by Site and Flow Condition

5.4 PCBs

Table 9 summarizes total PCB concentrations by site and flow condition, while individual data are presented in Figure 9.[2] Five to 35 of the 209 measured congeners were detected in each sample. In all but one sample (from Kanaskat-Palmer), detected PCB congeners were J-flagged as estimated values by the laboratory, because they were below the LMCL and above the SDL. Thus, there is some uncertainty in the total PBC values. During baseflow conditions, total PCB concentrations ranged from 11.8 picograms per liter (pg/L) at the Upper Green location to 33.7 pg/L at Sunday Creek. During storm events, total PCB

[2] See Section 5.5.1 and 5.6.2 for a description of additional PCB congeners not included in total PCB calculations due to equipment blank contamination concerns.

concentrations ranged from 18.2 pg/L at the Upper Green location to 149 pg/L at Kanaskat-Palmer. Total PCB concentrations at Kanaskat-Palmer were generally within the range of concentrations found at the sites above the Dam; however, the two highest storm event concentrations were observed at Kanaskat-Palmer.

Table 9. Summary of Total PCBs (pg/L) data by site and flow condition

Site	Flow	FOD	Min		Max		Average		Median	
Upper Green	Base	3/3	11.8	J	23.2	J	18.4	J	20.3	J
	Storm	3/3	18.2	J	99.7	J	53.9	J	43.9	J
Sunday Creek	Base	3/3	13.2	J	33.7	J	22.2	J	19.6	J
	Storm	3/3	19.9	J	54.7	J	38.9	J	42.1	J
Kanaskat-Palmer	Base	3/3	18.1	J	30.2	J	26.0	J	29.6	J
	Storm	5/5	27.5	J	149	J	75.4	J	32.6	J

FOD frequency of detection; J – estimated value

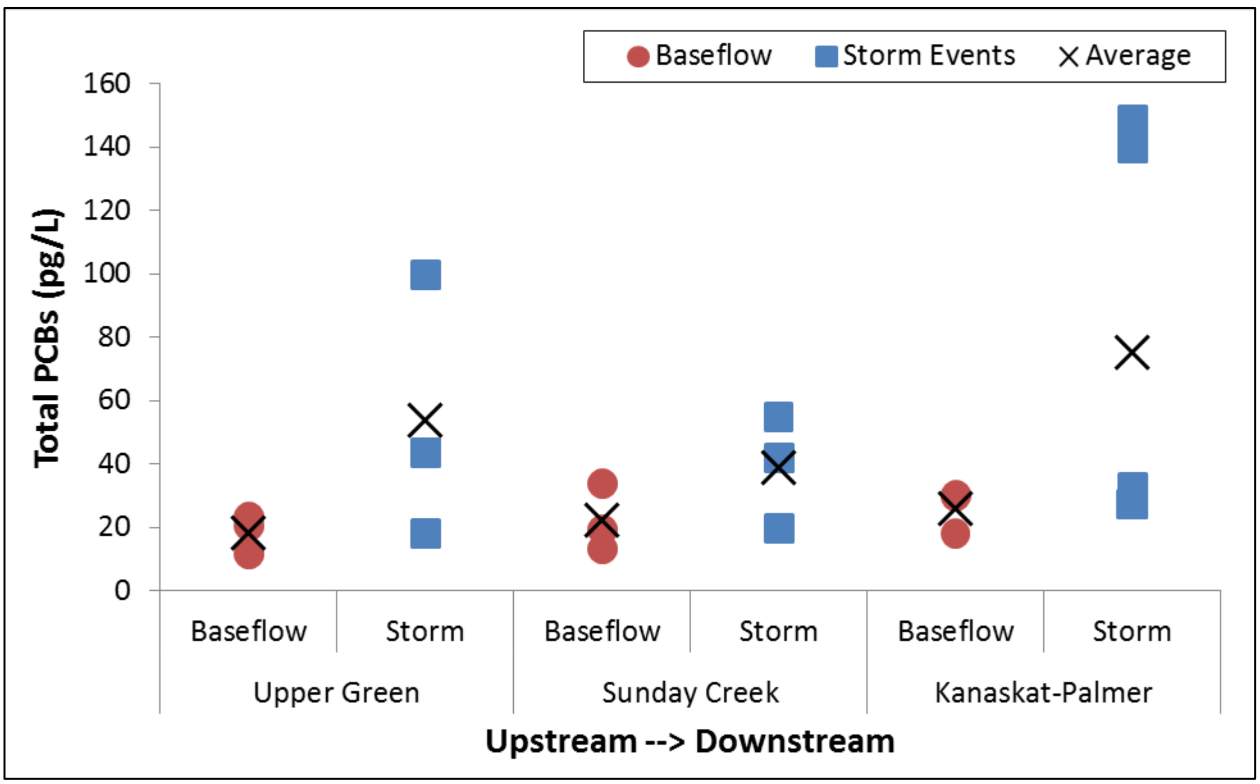

Figure 9. Total PCBs by Site and Flow Condition

5.5 Quality Control/ Quality Assurance Samples

This section presents the results for equipment blank and field replicates for arsenic, total LPAHs and HPAHs, total PCBs and conventional parameters. Results for all parameters are summarized in Appendix B.

5.5.1 Equipment Blank

Equipment blank samples provide an indication of potential chemical contamination associated with field equipment. They can help detect false positives or results that may have a high bias by identifying if chemical contamination is associated with sampling and storage equipment. One equipment blank was collected using an ISCO autosampler and analyzed for all study parameters. As noted in Section 2.2, results for this equipment blank only apply to Kanaskat-Palmer samples because autosamplers were not deployed at the Sunday Creek and Upper Green location. Table 10 presents the equipment blank results. With the exception of one LPAH (naphthalene; 0.0121 µg/L), arsenic, HPAHs, LPAHs, and TSS were not detected in this sample. Naphthalene was also detected in laboratory method blank samples, but concentrations were almost an order of magnitude lower than the equipment blank concentration. For the majority of environmental samples, naphthalene concentrations were two or more times the equipment blank concentration; however, naphthalene concentrations may be biased high in Kanaskat-Palmer data based on the equipment blank results.

Table 10. Equipment blank results

Group	Compound	Blank result	Qualifier	Units
Conventionals	Total Organic Carbon	0.5	U	Mg/L
	Dissolved Organic Carbon	0.5	U	Mg/L
	Total Suspended Solids	0.5	U	Mg/L
Arsenic	Total Arsenic	0.1	U	µg/L
	Dissolved Arsenic	0.1	U	µg/L
LPAHs	2-Methylnaphthalene	0.00283	U	µg/L
	Acenaphthene	0.00033	U	µg/L
	Acenaphthylene	0.00024	U	µg/L
	Anthracene	0.00024	U	µg/L
	Fluorene	0.000943	U	µg/L
	Naphthalene	0.0121		µg/L
	Phenanthrene	0.00189	U	µg/L
	Total LPAHs	0.0121		µg/L
HPAHs	Benzo(a)anthracene	0.00024	U	µg/L
	Benzo(a)pyrene	0.00047	U	µg/L
	Benzo(b,j,k)fluoranthene	0.00047	U	µg/L
	Benzo(g,h,i)perylene	0.00028	U	µg/L
	Chrysene	0.00024	U	µg/L
	Dibenzo(a,h)anthracene	0.00033	U	µg/L
	Fluoranthene	0.000943	U	µg/L
	Indeno(1,2,3-Cd)Pyrene	0.00033	U	µg/L
	Pyrene	0.000943	U	µg/L
	Total HPAHS	0.000943	U	µg/L

Group	Compound	Blank result	Qualifier	Units
PCBs	Total PCBs	197 [a]	J	pg/L

U – non-detect; J – estimated value
[a] Coeluting congener groups PCB-44/47/65. PCB-45/51, and PCB-68 comprised 175 pg/L of this total.

The total PCB concentration in the single equipment blank sample was 197 pg/L. PCBs were also detected in the AXYS laboratory method blanks, associated with these samples, at concentrations ranging from 58 to 192 pg/L. When analyzing PCB congeners at such low detection levels (e.g., 1-10 pg/L), it is not uncommon to detect low levels of PCBs in laboratory method blanks. Data validation examined the method blanks relative to environmental samples in detail and these comparisons are described in Section 5.6 below. For another King County study (King County 2013f) the KCEL reverse-osmosis water, which is used for equipment blanks in this study, was analyzed for PCB congeners and had a total PCB concentration of 31.8 pg/L.

However, the equipment blank still exceeded these method blank and reverse-osmosis water sample results. Upon further review, the three coeluting congener groups with the highest detected concentrations in the equipment blank include the congeners indicative of contamination from silicone tubing (i.e., PCB-47, PCB-51, and PCB-68); these comprised 89% of the total PCBs. The remaining PCB total is similar to that observed in laboratory water used to generate the equipment blank. The equipment blank results and subsequent research (King County 2018) confirmed that the silicone tubing used in the autosampler influenced total PCB concentrations in study samples. The PCB totals presented in this study were adjusted to exclude the PCB congeners associated with silicone tubing used in sample collection and processing (See report cover sheet).

Appendix D includes further discussion of equipment blank or laboratory contamination, including congener profiles for equipment blanks, the KCEL reverse-osmosis water sample and environmental samples from the Green River watershed.

5.5.2 Field Replicates

Field replicate samples provide an indication of natural and analytical variability. Four field replicates were collected for this effort. One replicate each was collected during storm conditions at each of the three locations, while the fourth replicate was collected at the Upper Green location during baseflow conditions. To evaluate natural variability, relative percent differences (RPD) were calculated for each sample pair and are reported in Table 11.

Table 11. Comparison of field replicate results

Parameter	Kanaskat-Palmer -1/8/14 (Storm)					Sunday Creek -11/7/13 (Storm)				
	Sample		Replicate		RPD	Sample		Replicate		RPD
Conventionals (mg/L)										
TOC	1.10	J	1.05	J	**5%**	1.16		1.08		**7%**
DOC	0.86		0.98		**13%**	1.43		1.42		**1%**
TSS	9.80	J	12.7	J	**26%**	1.40		1.30		**7%**
Arsenic (µg/L)										
Total	0.50	J	0.49	J	**2%**	0.10	J	0.10	U	**0%**
Dissolved	0.36	J	0.34	J	**6%**	0.11	J	0.10	U	**10%**
LPAHs (µg/L)										
2-Methylnaphthalene	0.0014	J	0.0016	J	**13%**	0.00061	U	0.00061	U	**n/d**
Acenaphthene	0.00045	J	0.00039	J	**14%**	0.00033	U	0.00033	U	**n/d**
Acenaphthylene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Anthracene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Fluorene	0.00058	J	0.0006	J	**3%**	0.00024	U	0.00024	U	**n/d**
Naphthalene	0.0296		0.0475		**46%**	0.0613		0.051		**18%**
Phenanthrene	0.0019	U	0.00189	U	**n/d**	0.00189	U	0.00189	U	**n/d**
HPAHs (µg/L)										
Benzo(a)anthracene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Benzo(a)pyrene	0.00048	U	0.00047	U	**n/d**	0.00047	U	0.00047	U	**n/d**
Benzo(b,j,k)fluoranthene	0.00048	U	0.00047	U	**n/d**	0.00047	U	0.00047	U	**n/d**
Benzo(g,h,i)perylene	0.00029	U	0.00028	U	**n/d**	0.00028	U	0.00028	U	**n/d**
Chrysene	0.00024	J	0.00024	U	**0%**	0.00024	U	0.00024	U	**n/d**
Dibenzo(a,h)anthracene	0.00033	U	0.00033	U	**n/d**	0.00033	U	0.00033	U	**n/d**
Fluoranthene	0.000952	U	0.000951	U	**n/d**	0.000943	U	0.000943	U	**n/d**
Indeno(1,2,3-Cd)Pyrene	0.00033	U	0.00033	U	**n/d**	0.00033	U	0.00033	U	**n/d**
Pyrene	0.000952	U	0.000943	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Total PCBs (µg/L)	221	J	53.0	J	**123%**	14.2	J	21.6	J	**41%**

Parameter	Upper Green - 9/10/13 (Baseflow)					Upper Green - 10/1/13 (Storm)				
	Sample		Replicate		RPD	Sample		Replicate		RPD
Conventionals (mg/L)										
TOC	0.55	J	3.06		**139%**	2.16		2.14		**1%**
DOC	0.61	J	3.04		**133%**	2.07		2.16		**4%**
TSS	1.0	U	0.50	U	**n/d**	1.10		0.50	J	**75%**
Arsenic (µg/L)										
Total	0.15	J	0.14	J	**7%**	0.18	J	0.16	J	**12%**
Dissolved	0.15	J	0.14	J	**7%**	0.15	J	0.14	J	**7%**
LPAHs (µg/L)										
2-Methylnaphthalene	0.00283	U	0.00283	U	**n/d**	0.00077	J	0.00061	U	**23%**

Parameter	Upper Green - 9/10/13 (Baseflow)					Upper Green - 10/1/13 (Storm)				
	Sample		Replicate		RPD	Sample		Replicate		RPD
Acenaphthene	0.00033	U	0.00155	U	**n/d**	0.00033	U	0.00033	U	**n/d**
Acenaphthylene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Anthracene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Fluorene	0.0022	U	0.0022	U	**n/d**	0.00033	J	0.00026	J	**24%**
Naphthalene	0.0453		0.0580		**25%**	0.172		0.094		**59%**
Phenanthrene	0.00758	U	0.00283	U	**n/d**	0.00189	U	0.00189	U	**n/d**
HPAHs (µg/L)										
Benzo(a)anthracene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Benzo(a)pyrene	0.00047	U	0.00047	U	**n/d**	0.00047	U	0.00047	U	**n/d**
Benzo(b,j,k)fluoranthene	0.00047	U	0.00047	U	**n/d**	0.00047	U	0.00047	U	**n/d**
Benzo(g,h,i)perylene	0.00028	U	0.00028	U	**n/d**	0.00028	U	0.00028	U	**n/d**
Chrysene	0.00024	U	0.00024	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Dibenzo(a,h)anthracene	0.00033	U	0.00033	U	**n/d**	0.00033	U	0.00033	U	**n/d**
Fluoranthene	0.00255	U	0.00255	U	**n/d**	0.00031	J	0.00029	J	**7%**
Indeno(1,2,3-Cd)Pyrene	0.00033	U	0.00033	U	**n/d**	0.00033	U	0.00033	U	**n/d**
Pyrene	0.00134	U	0.00134	U	**n/d**	0.00024	U	0.00024	U	**n/d**
Total PCBs (µg/L)	48.2	J	6.47	J	**153%**	6.44	J	10.5	J	**48%**

RPD relative percent difference; n sample number; n/d non-detect;

U – non-detect; J – estimated value

PAHs were infrequently detected. The exception was naphthalene, which was consistently detected in both samples and replicates. While MDLs sometimes varied on a sample-by - sample basis, no RPD was reported for non-detects for both the primary and replicate samples in Table 11. With the exception of naphthalene, RPDs for detected individual PAH results were within the limits required for laboratory duplicate samples (<40% RPD) as described in the SAPs (King County 2013a, b). The laboratory RPDs for naphthalene matrix spike and spike duplicates ranged from 24-45%, similar to all but one of the field replicate RPDs. Arsenic reproducibility was very high, with all RPDs less than 20% as specified in SAPs for arsenic laboratory duplicates. The conventional parameters showed a wide range in RPDs with two TSS sample pairs and one TOC/DOC sample pair having RPDs greater than laboratory acceptance criteria.

For PCBs, two of the four sample pairs exceeded the laboratory duplicate acceptance criteria of 50% RPD[3]. In one pair (Kanaskat-Palmer storm sample), one sample had detections above the LMCL and the other had all detections below the LMCL. In all other sample pairs, detections were all below the LMCL. Congener results below the LMCL are

[3]For purposes of comparing laboratory duplicate RPD results to field replicate RPD results, the laboratory duplicate RPD was based total PCB sum; however, the SAP acceptance criteria for laboratory duplicates is applied on individual congeners during the data validation process.

considered estimates based on uncertainties in quantifying low-level concentrations. In these cases, there is more uncertainty in the RPD.

Overall, the field replicates indicate environmental variability may be high for TOC, DOC, TSS, and naphthalene, particularly in the Upper Green. The greatest RPDs were found in the baseflow sample pair collected at the Upper Green location. Results also indicate PCBs exhibit environmental variability at Kanaskat-Palmer during storm events. The degree of this variability is uncertain at the other sites due to low concentrations.

5.6 Chemistry Data Validation

Arsenic, PAH and conventional data were validated by King County using EPA National Functional Guidelines for Superfund data (EPA 2008 and 2010b) and project quality assurance limits outlined in the study SAPs. Validation details are described in a data validation technical memorandum (Appendix C). Validation of PCB congener data was completed by Laboratory Data Consultants, Inc. in accordance with EPA Superfund guidance (EPA 1995). PCB congener validation reports are provided in Appendix C. This section summarizes the major findings of the chemistry data validations.

5.6.1 Arsenic, PAHs and Conventional Parameters

KCEL reviewed the arsenic, PAHs and conventional parameter data by comparing the results to reference methods and SAP requirements, and flagging data with laboratory qualifiers where appropriate. Validation of these data was conducted by Water and Land Resources Division Science Section staff. The validation process included review of the data anomaly forms, batch reports and analytical quality control (QC) reports. The following QC parameters were also reviewed: holding time, method blanks, spike blanks and duplicates, matrix spikes and duplicates, laboratory duplicates and surrogates.

Most QC specifications were met; therefore, many analytes did not require qualifiers. However, some analytes were qualified with a J, indicating an estimated value or a U, indicating a non-detect. No data were rejected based on data validation. All analytical data are of acceptable quality based on the data validation findings. Issues that resulted in the qualification of data are summarized below.

In thirteen samples, DOC results were greater than TOC results. For two samples, the absolute difference between TOC and DOC concentrations was greater than the MDL and/or the RPD was greater than 20%, which represent the QC limits for laboratory duplicates for these analyses. Theoretically, DOC should always be less than or equal to TOC, as the dissolved portion is all or part of the total. Since differences between DOC and TOC in these samples were greater than expected due to analytical variability, TOC and DOC results in these two samples were qualified by the laboratory with a “J” flag and considered estimated with an unknown bias. These “J” flags were retained in the data validation process.

The analytical method for dissolved arsenic requires that samples be filtered within the method-specified 15-minute holding time. Due to travel time from the sampling site to the KCEL, it was not feasible to filter samples within the 15-minute holding time. As a result, all dissolved arsenic analyses were qualified with a "J" flag and considered estimated with an unknown bias. Method blanks most often had detections of fluoranthene, fluorene, naphthalene, phenanthrene, and pyrene.

Most results for fluoranthene, fluorene, phenanthrene, and pyrene were within five times the concentrations in the method blank, as a result, these data were qualified as non-detects. The naphthalene method blank detections were all less than five times the environmental detections and did not impact data usability. Appendix C describes the impacted work groups. Naphthalene was the only PAH with matrix spike or matrix spike duplicate recoveries outside of control limits. Naphthalene is more difficult to accurately quantify compared to other PAH compounds because it is much more volatile. While naphthalene results in only four samples were qualified as estimated (J flagged) with unknown or high bias due to matrix spike recovery issues, naphthalene results in all samples are expected to have greater variability than the other PAH compounds.

5.6.2 PCBs

PCB data were validated to Level III by Laboratory Data Consultants, Inc. Level III validation includes verification of custody, holding times, reporting limits, sample QC and QC acceptance criteria, frequency of QC samples, instrument performance checks, along with initial and routine calibration checks.

Holding time, initial and continuing calibrations and other instrument performance checks were all within method criteria. Internal standards experienced low recovery in one sample, which resulted in one congener detection flagged as estimated (J qualified).

Up to 19 PCB congeners were detected in method blanks, typically at low levels. The lowest detected PCB method blank contaminant was PCB-32 (0.844 pg/L) for work group 46443-101. The highest detected PCB congener in method blanks was PCB-11 (12.7 pg/L) in the same workgroup. Total PCBs detected in method blanks ranged from 58 to 192 pg/L. Environmental sample congener detections were qualified as non-detect whenever congener concentrations were less than five times the method blank concentration for that work group. The "5x rule" reduces the potential for false positives, but raises opportunities for false negatives. This potentially resulted in some low bias for congeners detected above the method blank concentration, but below five times the method blank. Because the Green River and Sunday Creek surface water samples had many low-level congener detections, a number of these detections with less than five times the method blank concentrations were qualified as non-detect.

Numerous PCB congeners were qualified by the analytical laboratory as "K" which means that not all identification and qualification criteria were met for these compounds. The maximum potential concentration is reported for "K" flagged congeners. These analytes were qualified as non-detects (U qualified) based on EPA Region 10 validation requirements.

An "R1" qualifier (data rejected) was added post-validation to identify coeluting congener groups that were heavily influenced by silicone tubing equipment contamination and excluded from total PCB calculations (i.e., PCB-44/47/65, PCB-45/51, and PCB-68) (King County 2018).

5.7 Precipitation and Flow Data

The storm events sampled during this project covered a range of storm conditions, ranging from 0.26 inches to 1.44 inches of total daily rainfall (Table 12). Average flow during storm events at Kanaskat-Palmer ranged from 867 to 2,310 cubic feet per second (cfs). At Sunday Creek and the Upper Green locations, storm flows ranged from 50.6 to 205 cfs; however, the storm event on November 18-19, 2013 resulted in flow conditions that were unsafe for flow measurements to be taken at these two locations. This event also resulted in the highest average flow measured at Kanaskat-Palmer during a sampling event. This storm is discussed in more detail in Section 6.4.

Baseflow conditions over the sampling period were less variable at Kanaskat-Palmer than at the sites above the Dam. However, at both Sunday Creek and the Upper Green locations, the late baseflow sample was collected during flow conditions that were about five times higher than earlier baseflow conditions (Table 12). This October event is considered a wet-baseflow condition. It is unclear how sampling under these conditions may have affected baseflow chemical characterization; however, no patterns are evident.

Because the Kanaskat-Palmer is downstream from the Dam, flow at this site is highly dependent on Dam releases. The previous Green River Surface Water Report (King County 2014a) considered flows over 2,000 cfs at the USGS gage below the Dam (#12105900) "significant" releases and this definition has been adopted for the current report as well. Significant releases occurred throughout two sampling events (April 11, 2013, and November 11, 2013), and occurred during a portion of two other sampling events (April 5, 2013, and April 19, 2013). Relationships between flow and contaminant concentrations at this site are discussed in Section 6.4.

Table 12. Rainfall and flow data for each sampling event

Site	Flow	Sample Collection End Date/Time	Duration (hours)	Total Rainfall (inches)		Flow (cfs)[c]		
						Min	Max	Mean
				Day Prior to Sampling[a]	Day of Sampling[a]			
Upper Green	Base	9/4/13 14:10	2	0.04	0	n/a	n/a	15.1
		9/10/13 15:07	2	0	0	n/a	n/a	16.3
		10/17/13 12:10	2	0	0	n/a	n/a	44.3
	Storm	10/1/13 14:00	2	1.45	0.40	n/a	n/a	122
		11/7/13 12:25	2	0.07	1.01	n/a	n/a	50.6
		11/19/13 13:30	2	1.05	0.41	n/a	n/a	n/a
Sunday Creek	Base	9/4/13 13:56	2	0.04	0	n/a	n/a	5.88
		9/10/13 15:02	2	0	0	n/a	n/a	9.07
		10/17/13 11:55	2	0	0	n/a	n/a	50.6
	Storm	10/1/13 13:50	2	1.45	0.40	n/a	n/a	205
		11/7/13 12:30	2	0.07	1.01	n/a	n/a	115
		11/19/13 13:20	2	1.05	0.41	n/a	n/a	n/a
				24 Hours Prior to Sampling[b]	During Sampling[b]			
Kanaskat-Palmer	Base	7/11/13 5:00	24	0	0	358	378	365
		9/11/13 10:35	24	0	0	253	300	289
		9/20/13 10:52	24	0	0	322	354	326
	Storm	4/5/13 11:30	23.5	0.03	1.01	1,960	2,170	1,970
		4/11/13 4:30	23.5	0.01	0.26	2,130	2,220	2,160
		4/19/13 14:30	23.5	0.01	1.19	1,120	2,200	1,380
		11/7/13 21:30	23.5	0.02	1.01	726	1,340	959
		11/19/13 12:04	24	0.67	0.56	1,920	3,220	2,310
		1/9/14 9:30	23.5	0.23	0.41	842	1,130	938
		1/30/14 0:30	23.5	0.45	1.51	604	1,060	867

[a] Rainfall data for Sunday Creek and Upper Green from NOAA, Lester rain gage (LSFW1); data only available as daily total.
[b] Rainfall data for Kanaskat-Palmer from WLR Black Diamond gage (BDIA); data provided in 15-min intervals.
[c] Flows for Sunday Creek and Upper Green based on a cross-sectional average of Swoffer meter measurements by KCEL field staff. Flow data for Kanaskat-Palmer from USGS gage # 12105900.
n/a – not available (see Section 2.3).

6.0. DISCUSSION

This section discusses the results and how they relate to the study questions, as well as a comparison of water quality data to Washington State water quality standards (WQS).

6.1 Comparison to Water Quality Standards

Of the chemicals analyzed in this study, WQS for the protection of aquatic life have only been promulgated for dissolved arsenic and total PCBs. The chronic WQS for dissolved arsenic is 190 µg/L and for total PCBs is 14,000 pg/L. All measured concentrations in this study were well below these standards.

For human health WQS, Washington State previously defaulted to criteria in 40 CFR 131.36. These criteria are known as the National Toxics Rule (NTR) and are promulgated by EPA. In November 2016, EPA set new human health WQS for toxics for Washington State. The designated uses of the Green River include drinking water and fish consumption; therefore, the detected results from this study have been compared to the "water and organism" criteria listed in the NTR and new WQS. Table 13 lists all applicable Aquatic Life Criteria, NTR and human health WQS. Note that the human health standard for arsenic is not included because it only applies to inorganic arsenic, which was not measured in this study.

Table 13. Applicable aquatic life WQS, NTR and human health water quality standards (µg/L unless noted otherwise)

Parameter	Aquatic Life Standards	Water and Organism Human Health NTR	Water and Organism Human Health Standard (WA State)[a]
Dissolved arsenic	190	n/a	n/a
Acenaphthene	n/a	n/a	30
Anthracene	n/a	9,600	100
Benzo(a)anthracene	n/a	0.0028	0.00016
Benzo(a)pyrene	n/a	0.0028	0.000016
Benzo(b)fluoranthene[b]	n/a	0.0028	0.00016
Benzo(k)fluoranthene[b]	n/a	0.0028	0.0016
Chrysene	n/a	0.0028	0.016
Dibenzo(a,h)anthracene	n/a	0.0028	0.000016
Fluoranthene	n/a	300	6
Fluorene	n/a	1300	10
Indeno(1,2,3-Cd)Pyrene	n/a	0.0028	0.00016
Total PCBs	14,000 (pg/L)	170 (pg/L)	7 (pg/L)

[a] Washington State human health criteria consistent with 40 CFR 131.45; criteria updated by US EPA on November 15, 2016.
[b] Reported value is the sum of b, j, and k isomers of benzofluoranthene
n/a – not available

In this study, all arsenic, PAH, and total PCB results were below both the available aquatic life WQS and NTR criteria. Total PCBs at all sites exceeded the new human health WQS of

7 pg/L. In addition, the one detection of indeno(1,2,3-Cd)pyrene exceeded the new human health WQS. Benzo(b)fluoranthene and benzo(k)fluoranthene could not be assessed because they are analyzed as benzo(b,j,k)fluoranthene. No other sample results exceeded the human health WQS. Figure 10 compares PCB results from the Upper Green Basin and Kanaskat-Palmer sites to the NTR and human health WQS.

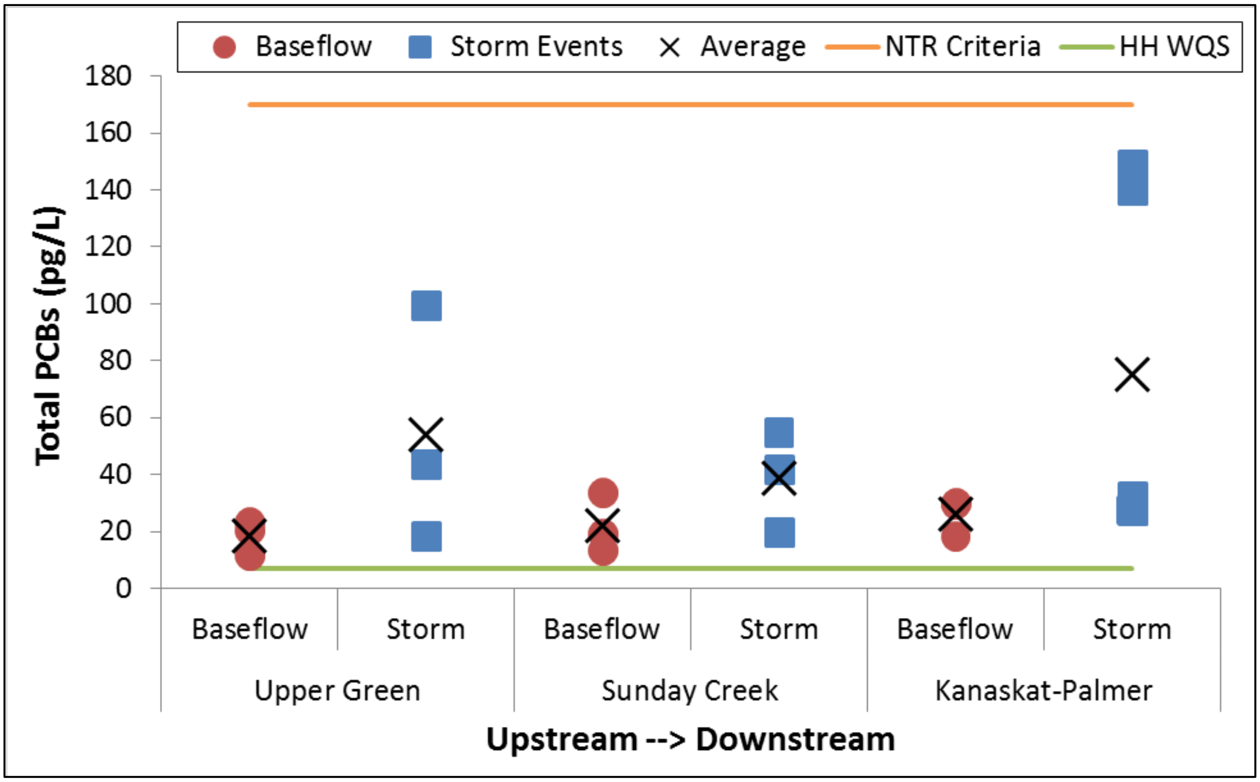

Figure 10. Upper Green River Basin and Kanaskat-Palmer PCB concentrations compared to NTR and human health water quality standard.

6.2 Baseflow versus Storm Event Conditions

To analyze differences between parameter concentrations during baseflow and storm conditions, Sunday Creek and Upper Green data were combined (herein referred to as the combined Upper Green Basin sites) to increase sample size. Concentrations at these locations were quite similar; however, before the two data sets were combined, statistical analysis, using methods described in Section 4.3, was conducted to determine if results at these locations were significantly different. There was no statistical difference between these sites for parameters with greater than 75% FOD. In most cases, however, there was low statistical power due to the small sample size (i.e., probability of detecting an existing difference was low). Non-detects values were substituted at their detection limit values, but only for parameters with greater than 75% FOD. Section 4.3 includes additional details about the statistical analysis methods. Table 14 lists the statistical tests and results of baseflow versus storm event condition for Kanaskat-Palmer and the combined Upper Green River Basin locations.

Table 14. T-Test Results – Comparison of Baseflow to Storm Event Concentrations at Kanaskat-Palmer and the Combined Upper Green Basin Sites

	Kanaskat-Palmer			Combined Upper Green Basin		
Parameter	Difference	Test type	Significant	Difference	Test type	Significant
TOC	none	Parametric	No	none	Parametric	No
DOC	none	Parametric	No	none	Parametric	No
TSS	none	Parametric	No	n/a	n/a	FOD < 75%
Total Arsenic	Base > Storm[a]	Parametric	**Yes, $p < 0.001$**	n/a	n/a	FOD < 75%
Dissolved Arsenic	Base > Storm[a]	Non-parametric	**Yes, $p < 0.01$**	n/a	n/a	FOD < 75%
LPAH	none	Parametric	No	none	Parametric	No
HPAH	n/a	n/a	FOD < 75%	n/a	n/a	FOD < 75%
PCBs	none	Parametric	No	none	Non-parametric	No

n/a - not applicable; test not performed due to low frequency of detection (FOD)
[a] ">" denotes which mean/median was greater, but the two-tailed t-tests only determine if there is a statistical difference between the means/medians, not which is statistically greater.

Total organic carbon and DOC concentrations were not significantly different between baseflow and storm conditions at either location; however, statistical power was low. A similar pattern was observed for TSS at Kanaskat-Palmer. For the combined Upper Green Basin sites, statistical differences in TSS could not be evaluated because of low FOD. Even so, at the combined Upper Green Basin sites, TSS concentrations were non-detect (average MDL of 0.7 mg/L) during baseflow conditions compared to an average detected concentration of 5.9 mg/L during storm event conditions.

Total and dissolved arsenic concentrations at Kanaskat-Palmer were significantly different during baseflow conditions relative to storm events. At the combined Upper Green Basin sites, FOD was less than 75%; therefore, statistical analysis was not performed. A visual comparison of detected arsenic concentration data at the Upper Green Basin sites shows overlap in baseflow and storm event concentrations at these locations (see Figures 5 and 6).

Total LPAH concentrations were not significantly different between baseflow and storm conditions at either location. HPAHs were not included in this analysis because of low FOD. A visual comparison of total LPAHs shows overlap in baseflow and storm event concentrations at all locations (see Figure 7).

Total PCB concentrations between baseflow and storm event conditions were not statistically different at either location; however, statistical power was low at Kanaskat-Palmer.

6.3 Kanaskat-Palmer versus the Combined Upper Green

To determine if results at Kanaskat-Palmer were significantly different than those at the combined Upper Green Basin sites, statistical analyses were conducted using the tests described in Sections 4.3 and 6.2. Baseflow results and storm results were considered separately. Table 15 summarizes the statistical results.

Table 15. T-Test Results - Comparison of Parameter Concentrations between Kanaskat-Palmer and the Combined Upper Green Basin Sites

	Baseflow			Storm Events		
Parameter	**Difference**	**Distribution**	**Significant**	**Difference**	**Distribution**	**Significant**
TOC	none	Parametric	No	none	Parametric	No
DOC	none	Parametric	No	Upper > KP[a]	Parametric	**Yes, $p < 0.01$**
TSS	n/a	n/a	FOD < 75%	none	Non-parametric	No
Total Arsenic	n/a	n/a	FOD < 75%	KP > Upper[a]	Non-parametric	**Yes, $p < 0.01$**
Dissolved Arsenic	n/a	n/a	FOD < 75%	KP > Upper[a]	Non-parametric	**Yes, $p < 0.01$**
LPAH	none	Parametric	No	none	Parametric	No
HPAH	n/a	n/a	FOD < 75%	n/a	n/a	FOD < 75%
PCBs	None	Parametric	No	None	Parametric	No

KP - Kanaskat-Palmer
Upper – combined Upper Green Basin sites
n/a - not applicable; test not performed due to low FOD
[a] ">" denotes which mean/median was greater, but the two-tailed t-tests only determine if there is a statistical difference between means, not which is statistically greater.

The only significant difference identified for the conventional parameters was for DOC during storm events; however, statistical power was low. During baseflow conditions, FOD for TSS was low; therefore, statistical analyses were not performed for these data.

Total and dissolved arsenic concentrations during storm events were significantly different between Kanaskat-Palmer and the combined Upper Green Basin sites. The FOD for total and dissolved arsenic was low during baseflow conditions; therefore, statistical analysis was not performed. However, concentrations at Kanaskat-Palmer were greater by a factor of three to four when compared to detected concentrations at the Upper Green Basin sites.

LPAH concentrations during either baseflow or storm event conditions were not significantly different between Kanaskat-Palmer and the combined Upper Green Basin sites. Differences in HPAH concentrations were not assessed due to low FOD.

PCB concentrations were not significantly different between Kanaskat-Palmer and the combined Upper Green Basin sites during either baseflow or storm conditions; however, statistical power was low.

6.4 Parameter Concentration and Flow

The November 18–19, 2013 storm event resulted in the highest flow during a sampling event over the study period.[4] The highest TSS concentrations at all sites were detected during this event. Elevated TSS concentrations can occur during higher flows because large rain events may wash off particles from upland areas (particularly impervious), and cause significant erosion or re-suspension of sediment bed particles. Once entrained, particulates are less likely to settle out of the water column during periods of high velocity. The maximum HPAH detection (see Table 8; Figure 8), a concentration six times higher than any other sample, was detected at Kanaskat-Palmer during this event.

Dissolved arsenic concentrations at Kanaskat-Palmer during storm events were moderately related to flow; concentrations decreased with increasing flow rates (Linear Regression $R^2 = 0.75$ and 0.60, respectively). Total PCB concentrations were relatively low and were not strongly related to flows at Kanaskat-Palmer ($R^2 = 0.27$). Flow is highly dependent on Dam releases at the Kanaskat-Palmer site. Significant releases from the Dam likely dilute any influence of local runoff, resulting in lower contaminant concentrations. For example, the two highest PCB concentrations at Kanaskat-Palmer were observed during storms with moderate flows (<1,000 cfs), suggesting local runoff may be an important contributor to storm event associated concentrations.

6.5 Comparison to Downstream Sampling Effort

In a previous sampling effort (King County 2014a), whole water samples were collected from two Green River mainstem sites downstream of the current study (Flaming Geyser [RM 41] and Foster Links [RM 10]) (Figure 11). The contributing basin to the Flaming Geyser site is more rural than the contributing basins to Kanaskat-Palmer. The contributing basin to the Foster Links site is more urban than any of the upstream site basins. One goal of the current study was to understand the relative concentrations of contaminants along the Upper and Middle Green River, which ultimately contributes to the Lower Duwamish Waterway. This section compares data from all four[5] Green River sites, and presents

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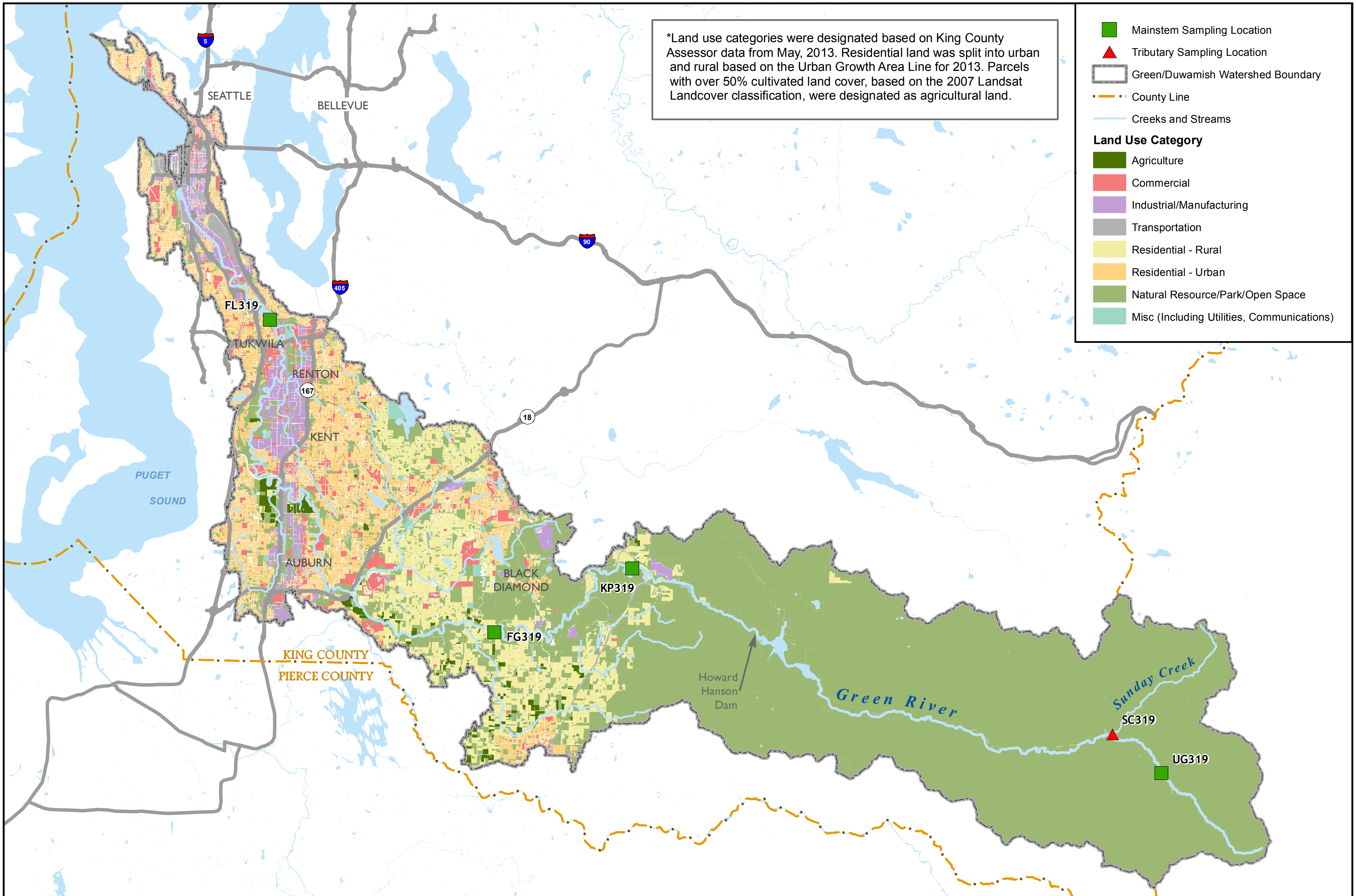
[4] Flow was not measured at the Upper Green Basin sites during this storm because of safety concerns due to the severely high flows (see Section 2.3).

[5] Both locations above Howard Hanson Dam (Upper Green and Sunday Creek) were combined for this analysis and considered as one Upper Green Basin site.

statistical results for differences between storm event concentrations, as described in Section 4.3. Baseflow data were not statistically analyzed due to low sample size (n=3 at each location).

TOC and DOC concentrations in storm event samples at the most downstream site (Foster Links) were significantly different from concentrations at Kanaskat-Palmer. No other statistical differences were found between sites. [6] Figure 12 illustrates these results.

[6] While the t-test analysis showed statistical differences in storm event DOC concentrations between the combined Upper Green Basin sites and Kanaskat-Palmer, this difference was not seen with ANOVA evaluations comparing all four mainstem sites. This was also true for total arsenic and total PCBs. T-tests are used to compare two sites, and ANOVAs are used to compare multiple sites. Results may differ, due to differences in statistical power.



King County
Department of
Natural Resources and Parks
Wastewater Treatment Division

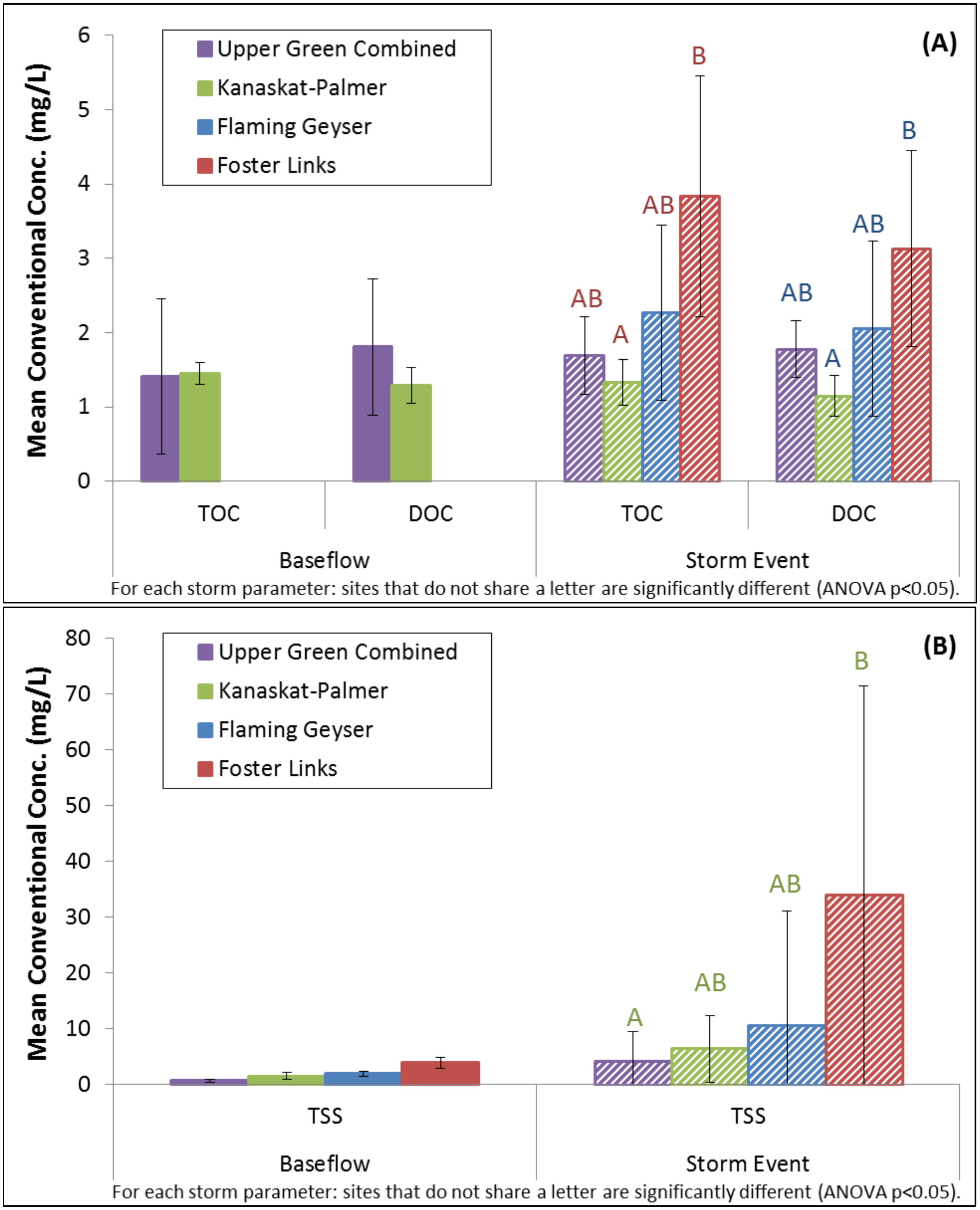
File Name: Q:\WTD\Projects\GreenDuwamish\Projects\2013WaterReport\LandUse10_H2O_85x11.mxd oneilsh

Data Source:

February 2015

Figure 11

Sampling Locations And Land Use In The Green/Duwamish Watershed

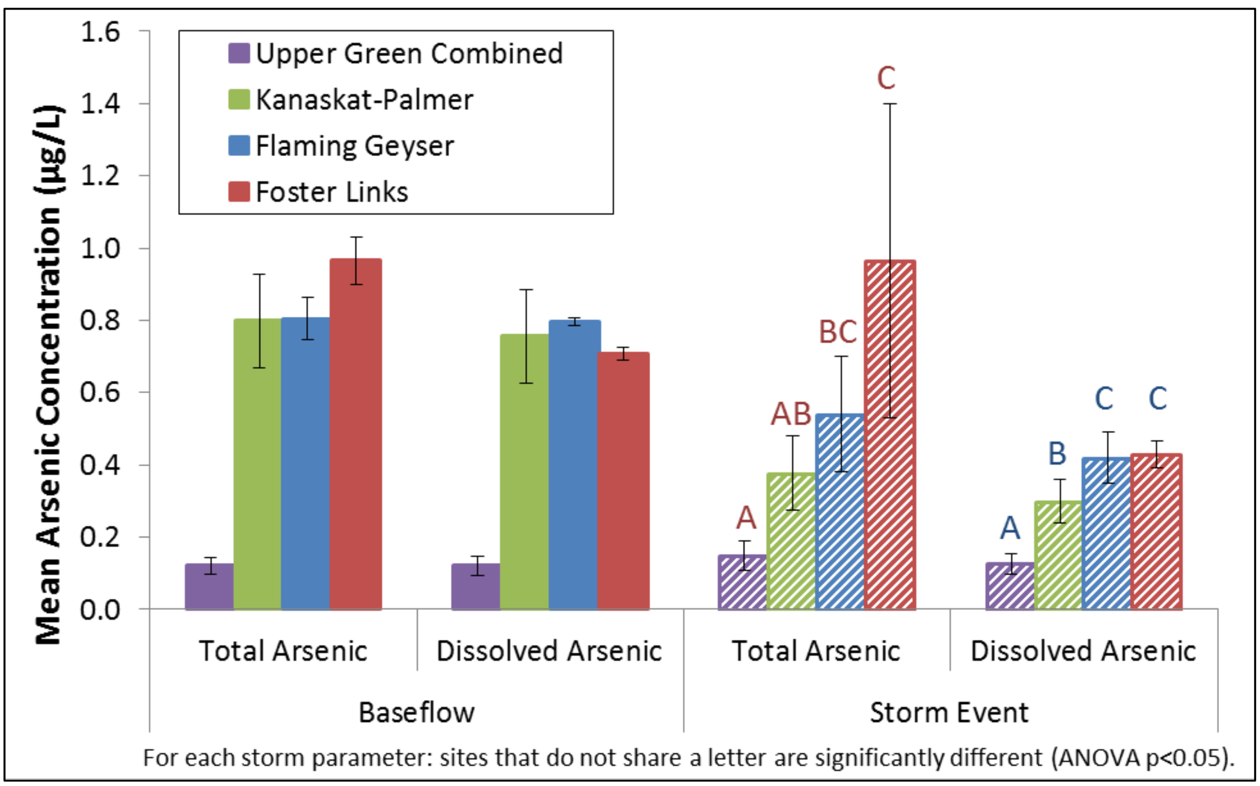


Error bars are standard deviations.
TOC and DOC baseflow data were not available for Flaming Geyser and Foster Links.

Figure 12. Comparison of conventional parameters in the Green River by flow condition – ANOVA results for storm events (*Left to Right: Upstream to Downstream*): (A) TOC and DOC; (B) TSS

There is increased variability of storm event TSS concentrations (see error bars representing standard deviations in Figure 12) moving from the Upper Green Basin to the lower reach of the Green River. This variability may be influenced by the increasing degree of urban development and number of tributaries discharging into the 31 miles of river between sampling locations. TSS was only statistically different between the combined Upper Green and the most downstream site (Foster Links), likely due to the high variability. Average TOC and DOC increase from upstream to downstream below the Dam; however, these increases are slight relative to increases in average TSS, with only Kanaskat-Palmer and Foster Links differing significantly.

Based on a graphical comparison, total and dissolved arsenic during baseflow conditions vary only slightly downstream of the Dam (Figure 13). However, all concentrations were relatively higher when compared with the combined Upper Green Basin sites. During storm conditions, total arsenic varied between sites. Concentrations in the combined Upper Green Basin sites were statistically different from Flaming Geyser and Foster Links, while Kanaskat-Palmer was statistically different from Foster Links. Dissolved arsenic concentrations at the combined Upper Green Basin sites were significantly different than all other sites, and Kanaskat Palmer was significantly different than both of the two downstream locations.



Error bars are standard deviations.

Figure 13. Comparison of arsenic in the Green River by flow condition - ANOVA results for storm events (*Left to Right: Upstream to Downstream*)

The increase in total arsenic during storm events is similar to the pattern observed for TSS. Figure 14 illustrates the relationship between TSS and total arsenic concentrations at the Green River sites. This regression analysis suggests that, during storm events, TSS concentration may be influencing total arsenic concentration at some sites (Kanaskat-Palmer and Foster Links).

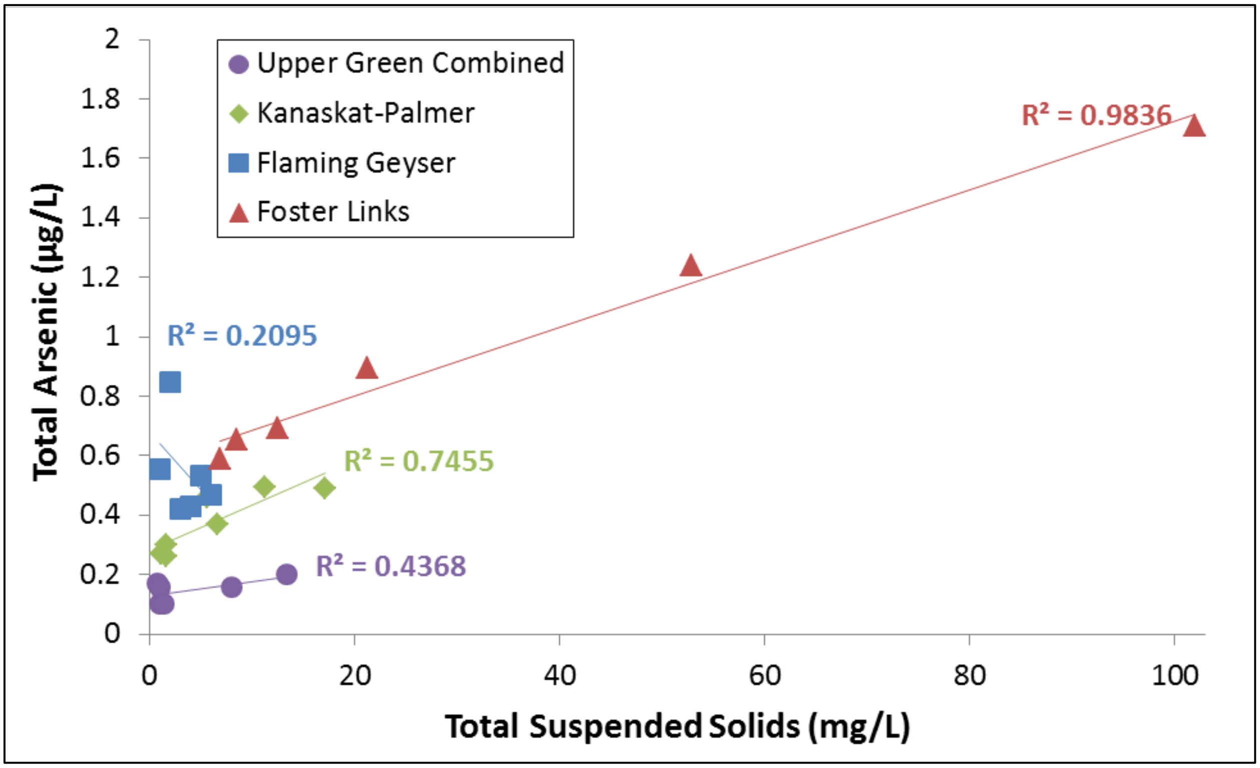
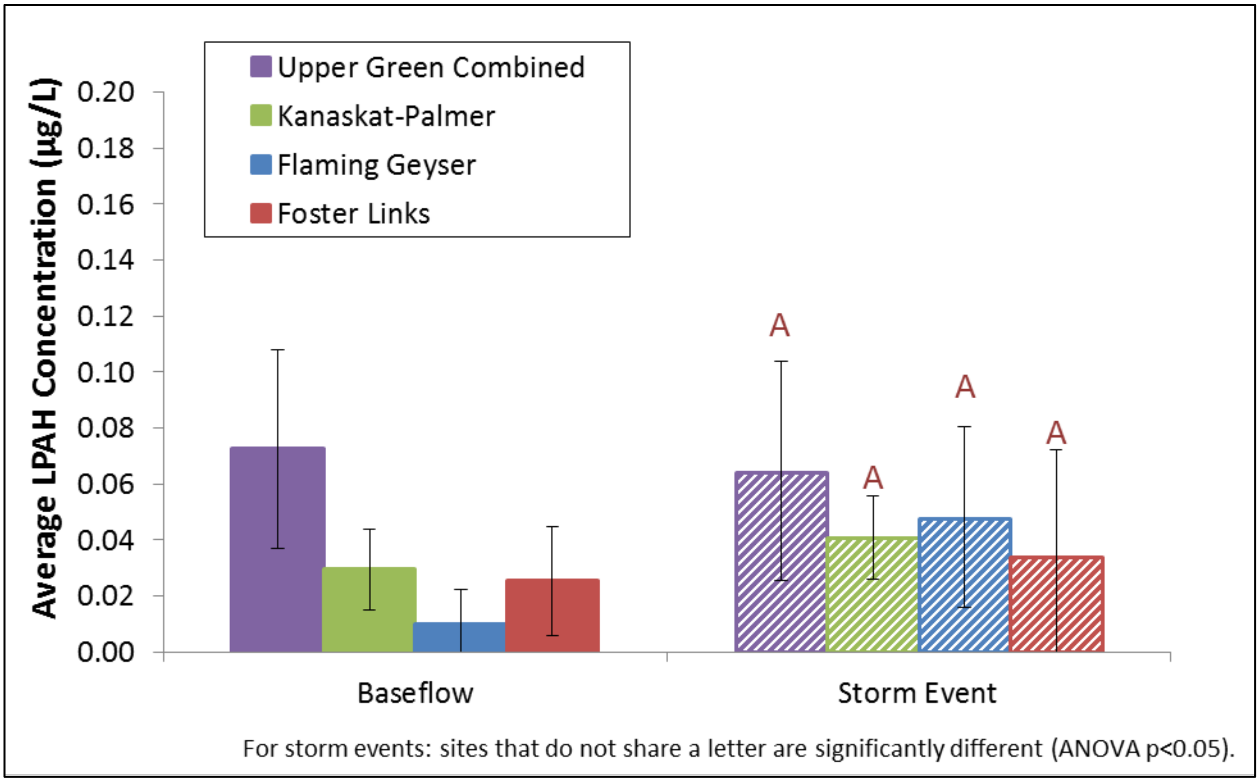


Figure 14. Storm event TSS and arsenic regression for Green River sites

Baseflow LPAH concentrations were quite variable, with the highest average total LPAH concentration, typically driven by naphthalene, measured at the combined Upper Green Basin sites. Storm event LPAH concentrations were not statistically different between sites. The high variability likely decreased the probability of identifying statistical differences (Figure 15). Average FOD for individual LPAH compounds was lowest (24%) at the combined Upper Green Basin sites[7]; however, at all sites, naphthalene comprises the largest proportion of total LPAH concentrations. As described in Section 5.6.1, naphthalene results should be interpreted with caution because of the high variability in naphthalene recovery due to its volatility.

[7] Average FOD for individual LPAH compounds were 45% at Kanaskat-Palmer, 31% at Flaming Geyser and 50% at Foster Links.

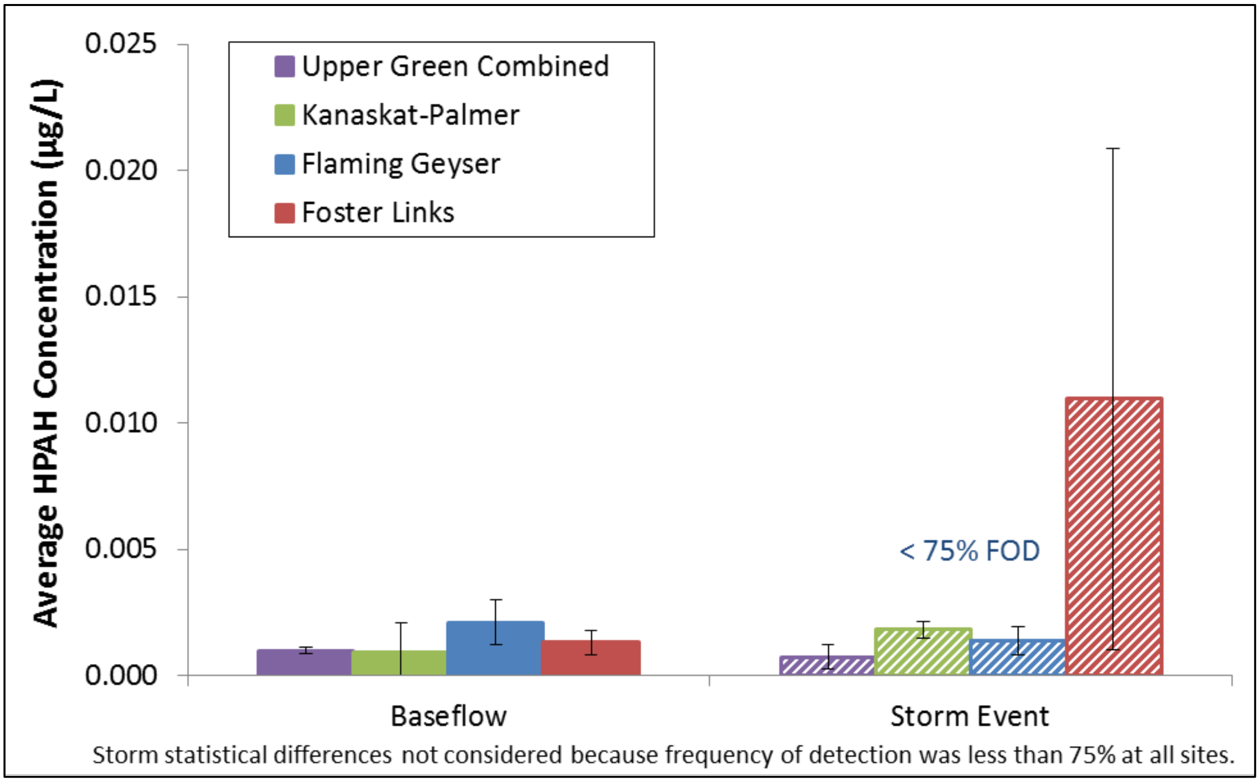


Error bars are standard deviations.

Figure 15. Comparison of Total LPAHs in the Green River by flow condition – ANOVA results for storm events (*Left to Right: Upstream to Downstream*)

Statistical differences were not considered for HPAHs due to low FOD. While the average total HPAH storm concentration at Foster Links was over ten times higher than any other Green River location, the data were highly variable, suggesting detection of statistical differences would be unlikely. The average FOD for individual HPAH compounds during storm events was lowest at the combined Upper Green Basin sites and highest at Foster Links[8]. Baseflow HPAH concentrations were generally similar between sites (Figure 16).

[8] Average FOD for individual HPAH compounds were 5% at the combined Upper Green Basin sites, 17% at Kanaskat-Palmer, 7% at Flaming Geyser, and 69% at Foster Links.

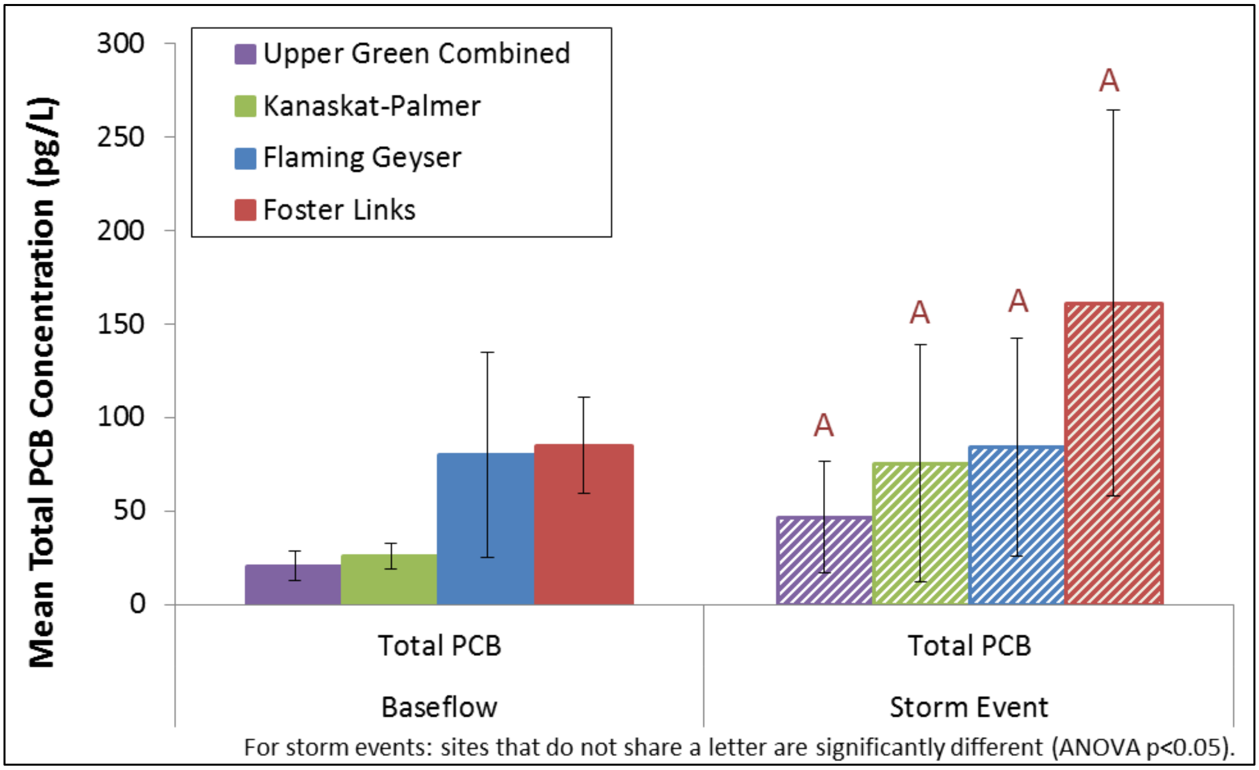


Error bars are standard deviations.

Figure 16. Comparison of Total HPAHs in the Green River by flow condition – ANOVA results for storm events (*Left to Right: Upstream to Downstream*)

Baseflow PCB concentrations were similar between sites, with slightly lower average concentrations detected at Kanaskat-Palmer and the combined Upper Green Basin sites. During storm events, average total PCB concentrations were lowest for the combined Upper Green Basin sites and highest at Foster Links. There were no statistical differences in average storm event concentrations between sites, although statistical power was low due to the relatively low sample size and high variability (Figure 17).

The relationship between total PCB and TSS concentrations were evaluated for storm events. The results of the regression analysis in Figure 18 illustrate there is no clear relationship between TSS and total PCB concentrations at the Green River sites. Other factors, such as land-use, local runoff during storm events, and influence of water releases from the Dam are likely influencing total PCB concentrations at these sites.



Error bars are standard deviations.

Figure 17. Comparison of Total PCBs in the Green River by flow condition – ANOVA results for storm events (*Left to Right: Upstream to Downstream*)

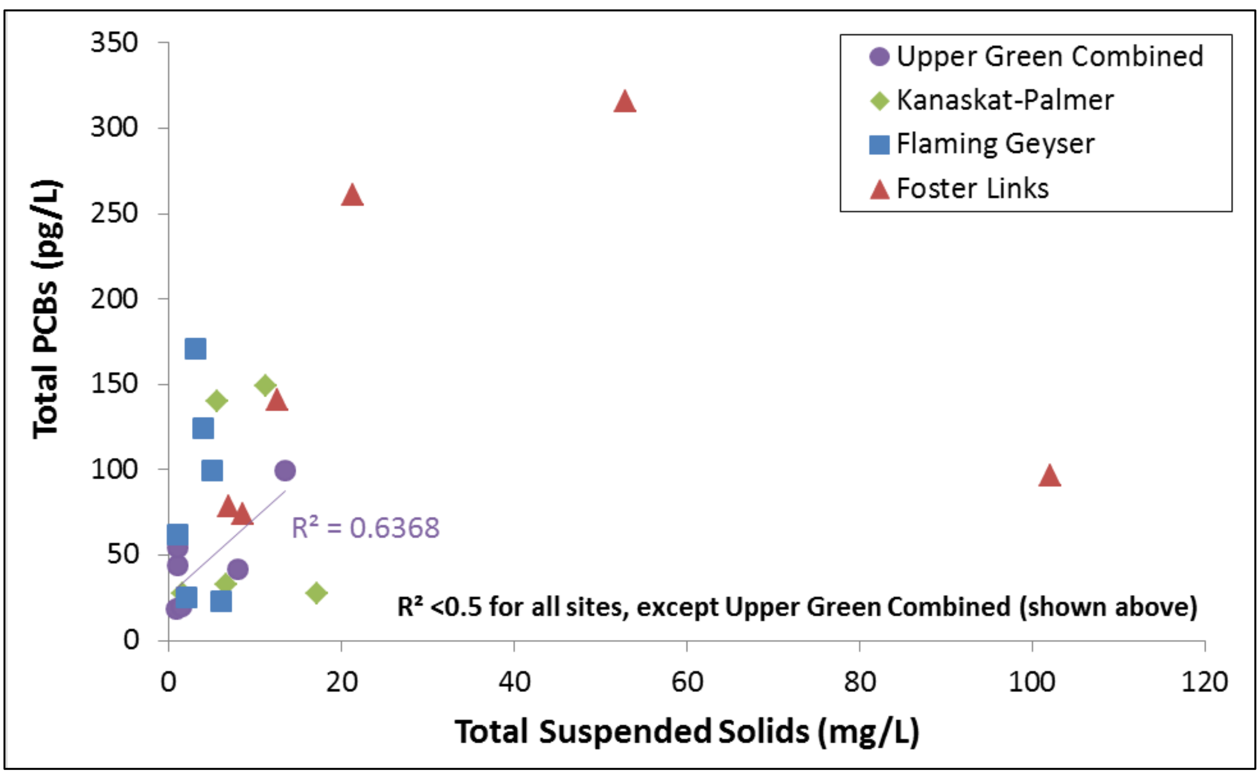


Figure 18. Storm event TSS and PCBs regression for Green River sites

7.0. CONCLUSIONS AND KEY FINDINGS

This report summarizes the results of surface water sampling and analysis from the Upper and Middle Green River basins to further evaluate contaminant concentrations in the upper reaches of the Green River, both above and below the Howard Hanson Dam. These data provide water quality information from areas further removed from development and urbanization than the Green River sampling locations previously evaluated (King County 2014a). These data allow King County and others to begin to characterize concentrations of LDW target contaminants from less developed portions of the watershed.

This study presents results of water quality samples collected and analyzed from three locations. The first two locations are located approximately 20 miles above the Dam; one on the mainstem Green River (RM 85) and a second on a major tributary, Sunday Creek (RM 82). The third site is located on the mainstem in the Middle Green Basin at Kanaskat-Palmer State Park, which is downstream of the Dam at RM 56.

Key findings of this study are presented below:

- The equipment blank results indicated that environmental samples collected with autosamplers were contaminated with PCBs and thus the results were biased high. A subsequent study (King County 2018) determined the type of silicone tubing used with the autosampler and sample splitting process was the source of the PCB contamination (i.e., congeners PCB-47, PCB-51, and PCB-68). Based on this, the PCB totals presented in this study were adjusted to exclude the PCB congeners associated with silicone tubing used in sample collection and processing.
- At Kanaskat-Palmer, total and dissolved arsenic concentrations were statistically different between baseflow and storm event conditions, with higher concentrations observed during baseflow. No other parameters (e.g., PCBs) with a FOD greater than 75% were statistically different between flow conditions at either Kanaskat-Palmer or the combined Upper Green Basin sites.
- During storm events, concentrations of total and dissolved arsenic were statistically different between Kanaskat-Palmer and the combined Upper Green Basin sites, with higher concentrations observed at Kanaskat-Palmer. DOC concentrations during storm events were statistically different between the sites, but higher concentrations were detected at the combined Upper Green Basin sites. PCB concentrations were not statistically different between locations.
- Storm event results at the combined Upper Green Basin sites and Kanaskat-Palmer were statistically compared to results from the previous sampling efforts further downstream on the Green River (i.e., Flaming Geyser State Park [RM 41] and Foster Links Golf Course [RM10]). During storm events, average concentrations of TSS, arsenic, total HPAHs and total PCBs generally increased from upstream to downstream. Statistical differences in storm event concentrations between sites were observed for TSS and arsenic. For most parameters, the increases were less pronounced during baseflow conditions, although statistical differences were not tested due to low sample size. These findings suggests that stormwater runoff from more developed downstream areas may be contributing to increasing contaminant

concentrations in the lower reaches of the Green river. Land use along the Green River shifts from forested watershed in the Upper Basin to urbanized land use in the Lower Basin.

- Dissolved arsenic and total PCB concentrations were well below Washington State WQS for the protection of aquatic life. Individual PAH and total PCB concentrations were below NTR criteria for human health, but total PCB concentrations at all sites were above the new Washington State human health WQS (as of 2016).

Statistical differences between baseflow and storm conditions for this study were only observed for arsenic at Kanaskat-Palmer. The lack of detectable differences between sites for other parameters could be due to low sample size or reduced contaminant input during storm conditions due to the limited development in the drainage basins contributing to these locations.

Additional targeted storm event sample collection in the Green River during periods of lower than average flow rates (e.g., during July–October) is recommended. Data collected when the Dam is not releasing a significant volume of water will allow for further evaluation of local runoff.

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