Lower Duwamish Waterway Source Control: Green River Watershed Surface Water Data Report

FINAL

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Department of Natural Resources and Parks
Water and Land Resources Division
Science and Technical Support Section
King Street Center, KSC-NR-0600
201 South Jackson Street, Suite 600
Seattle, WA 98104
206-477-4800 TTY Relay: 711
www.kingcounty.gov/EnvironmentalScience

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FINAL

Prepared for:

King County Wastewater Treatment Division
Department of Natural Resources and Parks

Submitted by: Carly Greyell, Debra Williston, and Deb Lester

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Citation

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Acronyms

µg/L	micrograms per liter
AXYS	AXYS Analytical Services
CFS	cubic feet per second
cm	centimeters
CSOs	combined sewer overflows
CVAF	cold vapor atomic fluorescence
DOC	dissolved organic carbon
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
FOD	frequency of detection
FSU	Field Science Unit
HPAHs	high molecular weight polycyclic aromatic hydrocarbons
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
KC	King County
KCEL	King County Environmental Laboratory
L	liter
LDC	Laboratory Data Consultants, Inc.
LDW	Lower Duwamish Waterway
LIMS	King County Laboratory Information Management System
LMCLs	lowest method calibration limits
LPAHs	low molecular weight polycyclic aromatic hydrocarbons
MDL	method detection limit
mg/L	milligrams per liter
mL	milliliter
MS	matrix spike
MSD	matrix spike duplicate
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
pg/L	picograms per liter

QA	quality assurance
QC	quality control
r^2	coefficient of determination
RDL	reporting detection limit
RI	remedial investigation
RO	reverse osmosis
RPD	relative percent difference
SAP	sampling and analysis plan
SDL	specific detection limit
SOP	standard operating procedure
SPE	solid-phase extraction
TOC	total organic carbon
TSS	total suspended solids
USGS	United States Geological Survey
WTD	King County Wastewater Treatment Division

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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. The water quality study presented here is one of these studies.

This study presents an assessment of water quality in the Green River Watershed to better understand the relative contribution of contaminants of concern for the LDW from upstream areas in the Green River. 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:

1) How do the relative contributions of arsenic, PAHs and PCBs differ between dry season/baseflow and wet season/storm conditions?
2) What are the relative spatial differences in arsenic, PAH and PCB concentrations in the Green River and its major tributaries?

This study includes collection and analysis of surface water samples from four major tributaries to the Green River (Newaukum, Soos and Mill creeks and the Black River), as well as at two locations on the main stem Green River: an upstream location at Flaming Geyser State Park (upriver of the tributary sampling sites), and a downstream location at Foster Links Golf Course (downstream of the tributaries). At each of the six locations, three composite samples were collected during the dry season to represent baseflow conditions, while six composite samples were collected during storm events. All 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 as a line-of-evidence to evaluate upstream contaminant sources to the LDW, improve the understanding and nature of these inputs (e.g., influence of storm events), and inform future source control efforts in the watershed.

This study also evaluated the ability of an ISCO® autosampler to collect a composite sample that was representative of conditions within the cross-section of the Green River. To do this, composite samples were collected at the Foster Links Golf Course location using two methods: (1) the same methodology described for this study (autosampler collection from one river location) and (2) grab samples from multiple locations over a river cross-section.

The study results indicate that for some parameters, significant[1] differences in concentration were observed between baseflow and storm event conditions. In addition, significant differences in concentration were also observed between some sampling

[1] Use of the term "significant" refers to a statistically significant difference based on a statistical analysis.

locations for TOC, DOC, total and dissolved arsenic, PCBs and HPAHs; no significant differences were observed between any location for TSS or LPAHs. Overall, concentrations of arsenic and total PCBs in the Green River study area are within the range or lower than those observed in a study that included the Puyallup and Snohomish watersheds. In both studies, detection frequencies for individual PAHs were low. The following bullets present additional detailed findings of the Green River water study.

Comparison of baseflow and storm event conditions:

- Total PCB, LPAH, HPAH and TSS concentrations were generally greater during storm events than under baseflow conditions. Significant differences between baseflow and storm event concentrations were observed at the Black River Pump Station for total PCBs, TSS, dissolved arsenic, and HPAHs and at Newaukum, Soos, and Mill creeks combined for TSS. Dissolved arsenic differed in the tributaries where there were significantly higher concentrations during baseflow compared to storm events.

Comparison between sampling locations:

- During storm events, mean TOC and DOC concentrations were highest in Mill Creek, which were significantly higher than concentrations in the two main stem Green River locations. TSS concentrations during storm events were highest at the Green River - Foster Links location, followed by Mill Creek; however, no significant differences were observed between any sites.

- During baseflow conditions, mean arsenic concentrations were within a factor of two at all sampling sites. During storm events, total and dissolved arsenic concentrations in Mill Creek were significantly higher than those detected in the two most upstream locations (Green River – Flaming Geyser and Newaukum Creek). During storm events, total arsenic concentrations in the Black River were also significantly greater than those in Newaukum Creek, as were dissolved arsenic concentrations in Mill Creek compared to the downstream Green River-Foster Links location.

- LPAH concentrations were variable across sites under both baseflow and storm event conditions and no significant differences were detected. Storm event HPAH concentrations were highest at the three most downstream locations: Mill Creek, Black River and the Green River - Foster Links location. During storm events, the highest HPAH concentrations were detected at the Black River Pump Station, which were significantly higher than concentrations measured at the three most upstream sites (Green River – Flaming Geyser, and Newaukum and Soos creeks).

- During storm events, total PCB concentrations were generally higher at the three most downstream locations: Mill Creek, Black River and the Green River - Foster Links location. PCB levels at the Black River Pump Station were significantly higher than at the Green River – Flaming Geyser site, Newaukum Creek, and Soos Creek. Under baseflow conditions, mean total PCB concentrations were highest in Soos Creek; however, elevated total PCB levels were detected in one sample and this data point greatly influenced the overall mean concentration.

- When storm event concentration data for the upstream and downstream Green River main stem locations were compared, significantly higher DOC, total arsenic and total HPAH concentrations were detected at the downstream location (Foster Links). No other significant differences were detected.

Evaluation of Sampling Methods:

- The comparison of sampling methods suggests that composite samples collected with the ISCO® autosampler deployed on the river bank are representative of conditions within the cross section of the Green River for all parameters except PCBs under baseflow conditions. The autosampler method yielded the higher PCB concentrations in both the baseflow and storm event sample pairs, with the most influential congeners including those indicative of contamination from silicone tubing (i.e., PCB-47, PCB-51, and PCB-68). After adjusting for the equipment contamination (see Section 5.6.1), storm event samples were comparable for the two methods, but baseflow samples still showed substantial differences, which could be due to environmental variability.

Collection of additional surface water data from the Green River Watershed is underway to further evaluate contaminant concentrations in the upper reaches of the Green River, both above and below the Howard Hanson Dam. Data collection from locations further upstream will provide additional water quality information from areas further removed from development and urbanization.

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 study presents an assessment of water quality in the Green River Watershed to better understand the relative contribution of contaminants of concern for the Lower Duwamish Waterway (LDW)[2] 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. The study was designed to address the following questions:

1) How do the relative contributions of arsenic, PAHs and PCBs differ between dry season/baseflow and wet season/storm conditions?
2) What are the relative spatial differences in arsenic, PAH and PCB concentrations in the Green River and its major tributaries?

This study includes collection and analysis of surface water samples from four major tributaries to the Green River, as well as at two locations on the main stem Green River: an upstream location at Flaming Geyser State Park (upriver of the major tributaries being sampled), and a downstream location at Foster Links Golf Course (downstream of the tributaries) (Figure 1). In addition to the questions listed above, the study also evaluated the ability of an ISCO® autosampler to collect a composite sample that was representative of conditions within the cross-section of the Green River. This data report presents and discusses the results of the 2011/2012 sampling program (King County 2011a) with respect to the questions posed 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); sampling evaluation method (Section 6.0); and discussion and conclusions (Section 7.0). Supporting appendices include chain of custody forms, laboratory data results, chemistry data validation reports, and correlation analyses.

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

1.1 Study Background

King County is a member of the Source Control Work Group (SCWG) for the LDW Superfund site. Other members include Washington Department of Ecology (Ecology; lead agency), the Environmental Protection Agency (EPA), City of Seattle, and the Port of Seattle. The SCWG 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 of the contaminants of concern identified in the LDW Superfund site that may contribute chemical inputs to the LDW and is currently conducting several studies to evaluate chemical concentrations in various media in the Green/Duwamish Watershed.

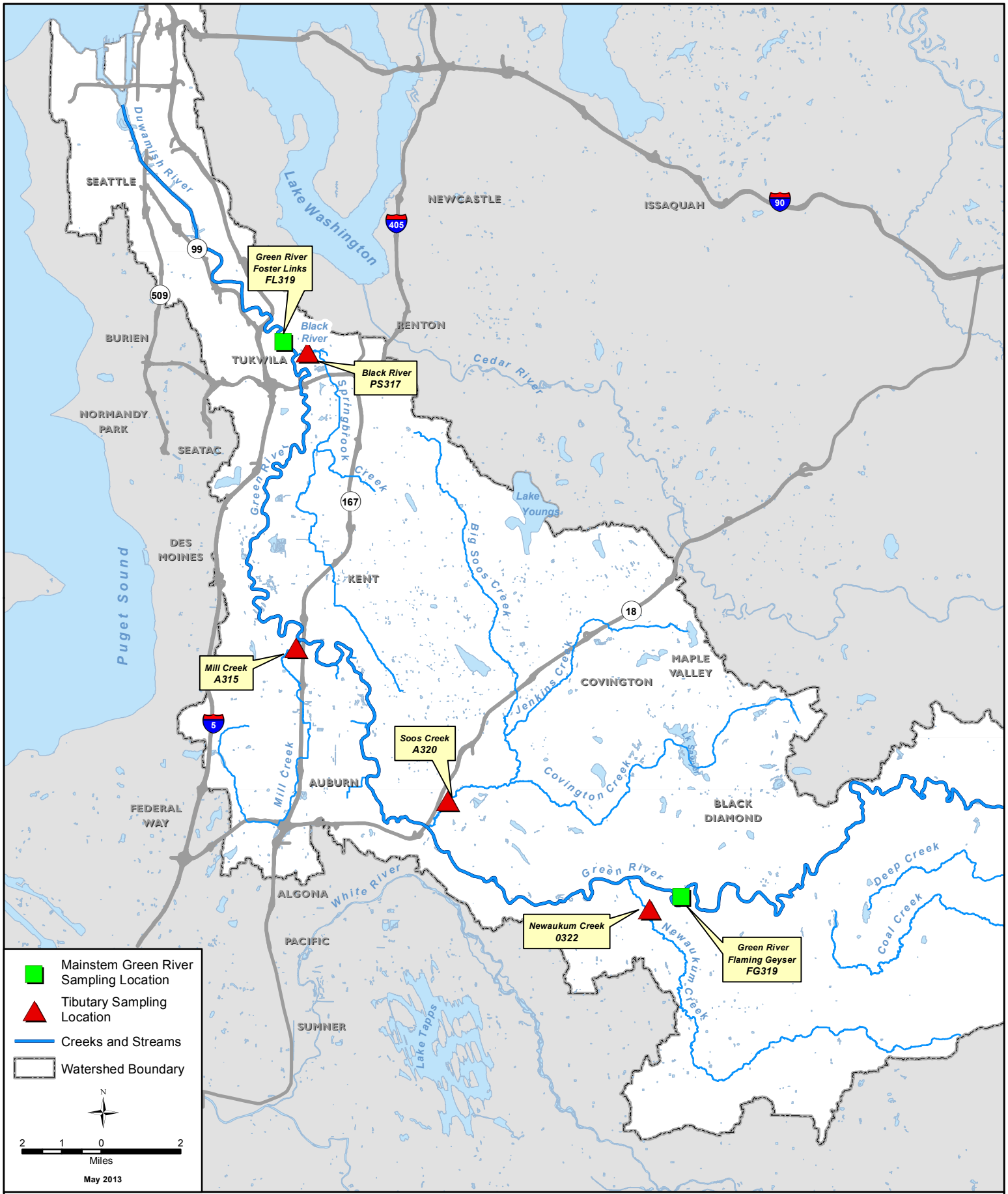

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Figure 1

Surface Water Sampling Locations

King County previously completed chemical analysis of whole water samples at a number of combined sewer overflows (CSOs) in the LDW Basin (King County 2011b) and has been characterizing solids within the combined sewer structures and lines that discharge to the LDW (King County 2011c). King County is currently conducting studies to evaluate chemical concentrations in sediment and suspended solids in the Green River Basin (King County 2012a, King County 2013a) and chemical mass flux in atmospheric deposition within the Green/Duwamish River Watershed (King County 2011d). The water quality study presented here is intended to complement data from these additional studies, as well as present a characterization of water quality for select parameters within the Green River Watershed.

The LDW Remedial Investigation (LDW RI) (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 (WQA) 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 main stem and associated tributaries were characterized in this 2005 study, additional data were deemed useful for comparison to past findings.

The purpose of this study is to provide a better understanding of the relative surface water concentrations of these contaminants, particularly PCBs and PAHs, from the major tributaries to the Green/Duwamish River. These data will be used as a line-of-evidence to evaluate upstream contaminant sources to the LDW, improve the understanding and nature of these inputs (e.g., influence of storm events), and inform future source control efforts in the watershed.

This study focuses on arsenic, PAHs, and PCBs because the LDW RI 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.

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 encompasses the Lower Green/Duwamish River and middle Green River portions of the Green/Duwamish Watershed and the following major tributary basins:

Newaukum, Soos and Mill Creeks and the Black River. The study area extends from the Green River at Flaming Geyser State Park (River Mile 41)[3] to the Green River[4] at Foster Links Golf Course (River Mile 10) and includes the major tributaries entering the Green River between these locations. The size of the drainage area included upstream of each Green River main stem sampling location and each tributary basin is shown in Table 1.

Table 1. Main Stem Green River and Tributary Basin Acreages for Each Sampling Location.

Site	Acreage
Main Stem Sites	
Green River – Flaming Geyser	166,028[a]
Green River – Foster Links	294,339[a]
Tributary Basins	
Newaukum Creek	17,280
Soos Creek	42,347
Mill Creek	10150
Black River	17,231

[a] Includes all upstream basins except closed systems (Coal and Deep Creeks)

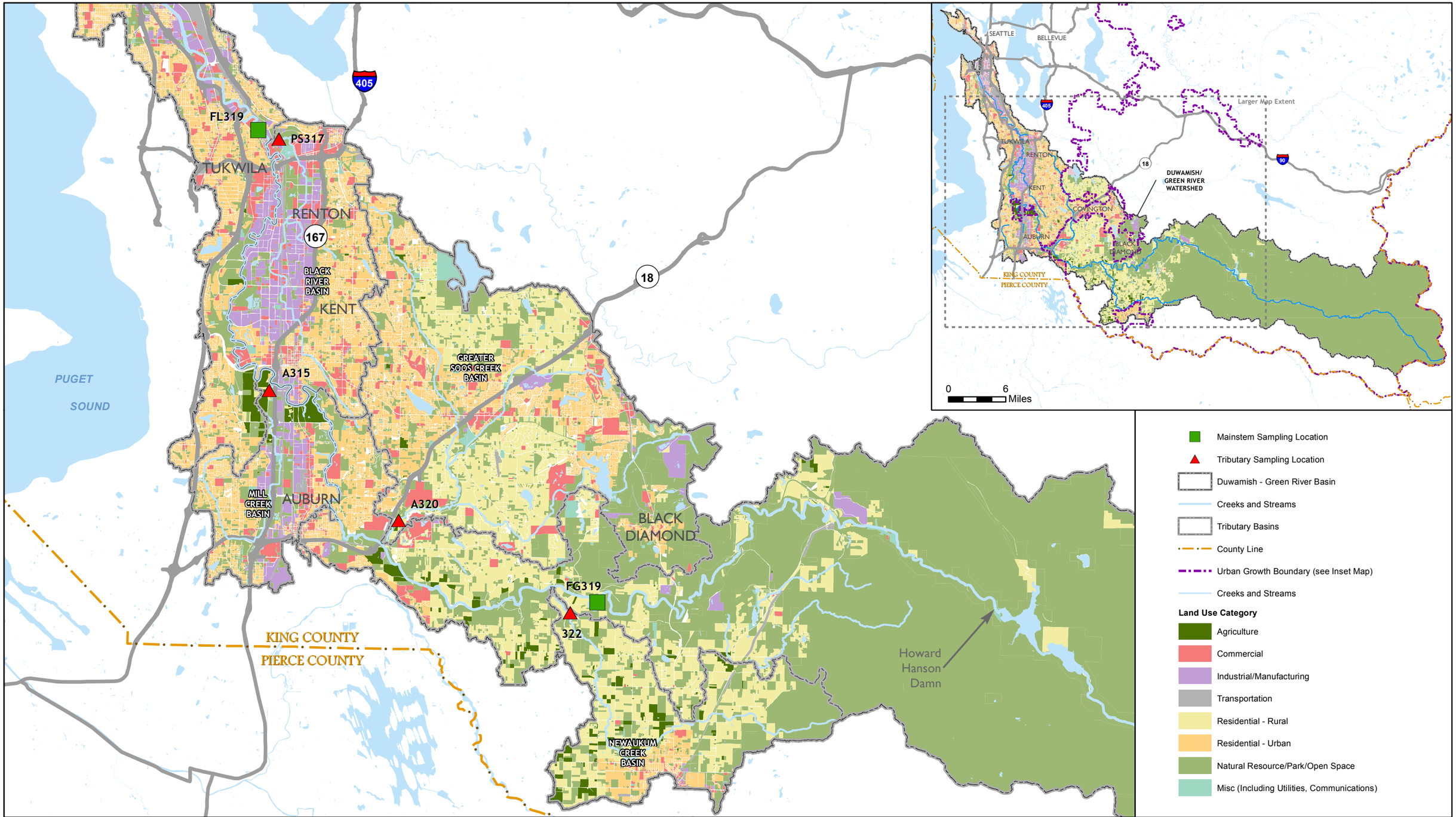
The Green-Duwamish Watershed encompasses a wide variety of current land uses[5] (Figure 2). Land use in the Upper Green River Basin, above the Howard Hansen Dam, consists of natural resource land: much of which is within a protected watershed that serves as a drinking water source. Land use in the middle Green River above Flaming Geyser State Park largely consists of natural resource/open space, in addition to some residential land use (Figure 2). Land use in the Newaukum and Soos creek basins is dominated by residential and natural resource/open space. However, the Soos Creek Basin also includes some commercial and utilities land use. Of the tributary basins, land use in the Black River and Mill Creek basins is the most diverse. The Mill Creek Basin consists of mixed land use with approximately 51% residential and natural resources, 13% manufacturing/industrial, 8% commercial and 6% agricultural land (Figure 3). The Black

[3] River mile designations are based on river mile 0 being at the southern end of Harbor Island; consistent with LDW site river mile designations.

[4] This area of the river is also referred to as the Duwamish River. The Duwamish River originates at the confluence of the Green and Black Rivers near Tukwila, Washington and flows northwest for approximately 19 km (12 mi), splitting at the southern end of Harbor Island to form the East and West Waterways, prior to discharging into Elliott Bay in Puget Sound, Seattle, Washington.

[5] Land use categories represent current use (i.e., were not based on zoned uses) and as such 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 Land Cover classification, were designated as agricultural land.

River Basin contains the largest percentage of commercial and manufacturing/industrial land (33%) (Figure 3). While land use in the area immediately adjacent to the Green River in the vicinity of the Foster Links Golf Course is dominated by residential land use, it also includes commercial and manufacturing/industrial uses (Figure 2). Land use in all of the upstream drainages is dominated by natural resource/open space and residential uses.



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**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.*

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Figure 2

Sampling Locations And Land Use In The Duwamish/Green Watershed

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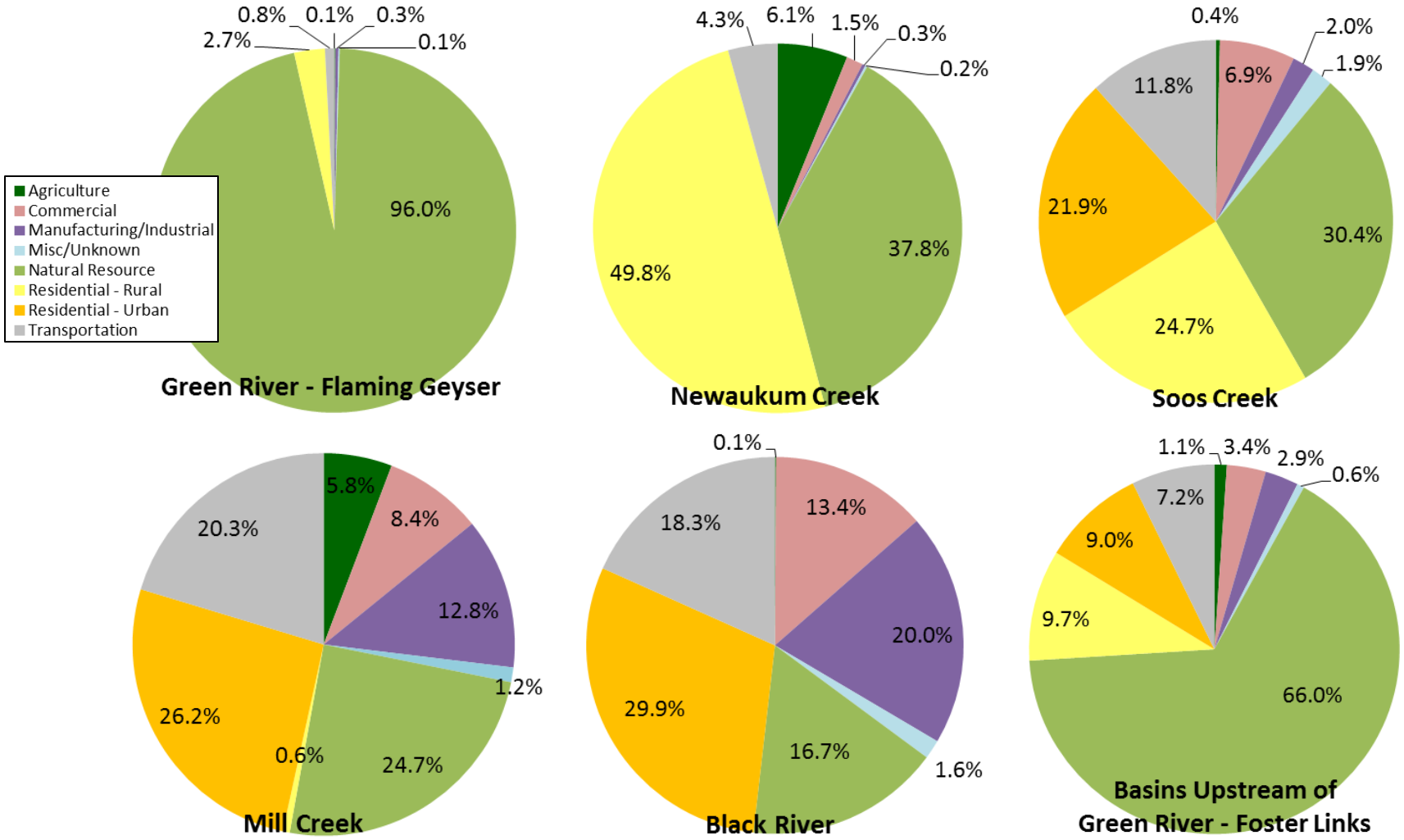


Note: land use associated with the Green River – Flaming Geyser and Green River – Foster Links sites is characterized as the entire watershed upstream of each of these locations (excluding closed systems).

Figure 3. Percent Current Land Use Associated with Each Sampling Site

2.0. FIELD SAMPLING METHODS

The following section provides an overview of the field sampling methods used in this study. The field procedures used to characterize concentrations of arsenic, PAHs and PCBs in surface waters from the Green River and four major tributaries are presented in greater detail in the study project Sampling and Analysis Plan (SAP) (King County 2011a), while field procedures to evaluate sampling methods are detailed in the SAP addendum (King County 2012b). The sampling locations are described in Section 2.1. Section 2.2 summarizes the flow data collection methods and Section 2.3 describes the sampling schedule and summarizes the collection methods. Section 2.4 summarizes the sample processing methods and finally, Section 2.5 describes deviations from the SAP encountered over the sampling period 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

Water samples were collected from six locations in the Green River Watershed during both dry season baseflow conditions and wet season storm events. Two sampling sites were located on the main stem Green River; an upstream location at Flaming Geyser State Park (upriver of the major tributaries being sampled), and a downstream location at Foster Links Golf Course in Tukwila (downstream of the tributaries) (Figure 1)[5]. Samples were also collected from four tributaries to the Green River: Newaukum, Soos and Mill creeks and the Black River at the pump station (Figure 1). The Black River Pump Station regulates discharge from the Black River at a dam located about 1000 feet above its confluence with the Green River. The pump station regulates flow of water from the Black River drainage basin into the Green River and serves to block high flows from the Green River from flooding up into the Black River, Springbrook Creek, and the Earlington Industrial Park in Renton. Water is discharged at this location through a series of pumps and a seasonal fish passage channel.

Samples from Newaukum and Soos creeks were collected near the mouth above their confluence with the Green River. During baseflow conditions samples from Mill Creek were collected downstream of the West Valley Highway bridge; storm event samples were collected on the upstream side of the bridge to avoid the influence of backwater conditions that can occur during high flows in the Green River.

Baseflow samples at the Black River Pump Station were collected from the fish passage channel. The fish passage channel is only operational during periods when fish passage is necessary (late summer, early fall); typically there is no flow through this channel during the wet season. The SAP (King County 2011a) specified that storm event samples would be collected from the Black River Pump Station on the downstream side of the dam during

[5] The Green River is often referred to as the Duwamish River at the confluence with the Black River. In this report, the main stem sampling location at Foster Links downstream of the confluence with the Black River is referred to as Green River rather than Duwamish River.

periods of pump operation. Unfortunately, pump operations were not predictable; therefore, the sampling location was shifted to the area just behind the dam (in the pooled area) at the depth of the pump intakes. The station coordinates, locators, and locator description associated with the six sampling locations are presented in Table 2. Samples to compare sampling methodologies were collected from the main stem Green River -Foster Links location.

Table 2. Green River and Tributary Sampling Locations and Locator Names

Locator	Locator Description	Approximate River Mile[a]	State Plane Northing[b]	State Plane Easting[b]
FG319	**Green River – Flaming Geyser** State Park, upstream location	41	104038	1341097
0322	Mouth of **Newaukum Creek**	40	102390	1336841
A320	Mouth of **Soos Creek**	33	116821	1309972
A315	**Mill Creek** in the vicinity of the West Valley Highway Bridge crossing	23	137218[b]	1289725[b]
PS317	**Black River** at the Black River Pump Station	10	176593	1291222
FL319	**Green River – Foster Links** Golf Course, downstream location	10	177997	1288012

[a]River Miles are based on south end of Harbor Island (lower boundary of LDW Superfund site) as river mile 0.0. Tributary river miles are approximately where they discharge into the Green River.

[b]Northing and easting at the Mill Creek site are approximate due to slightly different sampling locations for collection of baseflow and storm event samples.

2.2 Flow Data Collection

Flow data were collected or estimated at all sites during the sample collection period. Flow data at Newaukum and Soos creeks were based on US Geological Survey (USGS) gage data (Gage 12108500 and Gage 12112600, respectively); both gages are adjacent to the sample collection sites. Green River flow at Flaming Geyser was estimated based on the USGS gage below the Howard Hanson Dam (Gage 12105900), while flow at the Foster Links location was estimated based on flow at the USGS Auburn gage (Gage 12113000). A continuous flow gage in the vicinity of the Mill Creek sampling location has not been established. Therefore, flow during storm events was estimated using an ISCO® flow meter deployed during sampling. During baseflow events instantaneous flow was manually measured using a Swoffer flow meter just prior to and following completion of sample collection. Due to the relocation of the Black River sampling location described above in Section 2.1, it was not feasible to collect flow or discharge data at this site during storm events. Discharge from the fish passage channel at the Black River Pump Station during collection of baseflow samples was estimated based on the pumping rate. The flow data are presented in Section 5.7.

2.3 Sampling Schedule and Collection

All samples were collected according to methods described in the SAP (King County 2011a) and the SAP addendum (King County 2012b). Composite surface water samples were collected using ISCO® autosamplers equipped with 10-liter glass carboys. Teflon tubing was dedicated to each sampling location. Samples to evaluate the sampling methodologies were collected using both an autosampler placed in a single location and a Scott Bottle deployed at equal intervals over the cross-section of the river. Storm event sampling was triggered by specific rainfall conditions of at least 0.25 inch with a minimum 24-hour antecedent dry period. Samples were analyzed for arsenic, PAHs, PCB congeners, total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS).

The following rain gages, maintained by King County, were used to estimate precipitation in the vicinity of sampling locations:

- Black River Pump Station and main stem Green River at Foster Links Golf Course – TUKW (Tukwila)
- Mill Creek – SEQU (Sequoia Jr. HS, Kent)
- Soos Creek – 32U (Lower Green, N. Auburn)
- Newaukum Creek and main stem Green River at Flaming Geyser State Park - 40U (Middle Green)

Precipitation data associated with storm sampling events are presented in Section 5.7. The following sections provide a summary of the sample collection activities and schedule.

2.3.1 Green River and Tributary Surface Water Characterization - Baseflow Sample Collection

Three sets of baseflow samples were collected in September 2011 following a minimum 3-day antecedent dry period. All baseflow samples were 24-hour time-weighted composites where autosamplers were programmed to draw a sample aliquot at 30 minute intervals. Baseflow samples were collected at all six locations; samples at the Black River were collected from the fish passage channel which was representative of discharge from the Black River during the dry season (no other pumps were running during the collection period). The specific sample collection dates are presented in Table 3; a total of 18 baseflow samples were collected.

Table 3. Summary of Samples Collected during Baseflow Conditions

Location	2011						Total Count
	9/6	9/7	9/12	9/13	9/14	9/15	
Green River - Flaming Geyser		X	X	X			3
Newaukum Creek	X	X	X				3
Soos Creek	X	X		X			3
Mill Creek	X	X	X				3
Black River				X	X	X	3
Green River - Foster Links				X	X	X	3
Total Number of Baseflow Samples							**18**

2.3.2 Green River and Tributary Surface Water Characterization - Storm Event Sample Collection

Six 24-hour flow-weighted composite storm event samples were collected during the wet season (October through April) from each of three tributary locations (Newaukum, Soos and Mill). Collection of flow-weighted composite samples from the Black River was not appropriate because flow is managed by the pump station; time-weighted composite samples were collected from this location. All sampling was conducted for a maximum of 24 hours, with the exception of four events at Newaukum Creek, one event at Soos Creek and three events at Mill Creek (see Section 2.5).

As previously discussed, the Black River storm event sampling location was relocated to the pooled area behind the dam. The autosampler intake was located behind the dam near the intake for Pump #1 and programmed to collect 24-hour time-weighted composite samples (aliquots collected at 30 minute intervals). One field replicate was collected from the Black River.

Six storm event samples were collected from each of the two Green River main stem locations. Section 2.2 of the SAP specified that, if possible, three of the six storm samples were to be collected from the main stem Green River locations when the Howard Hansen Dam was not releasing a significant volume of water (assumed to be 2,000 cubic feet per second [cfs] based on flow at the USGS gage [12105900] below Howard Hanson Dam). All but two of the six samples from both main stem locations were collected when dam releases were less than 2,000 cfs (samples taken on 1/31/2012 and 2/24/2012 were collected during flows above 2,000 cfs). One field replicate sample was collected at the Green River –Flaming Geyser location. All main stem samples were collected as 24-hour time-weighted composites programmed to collect sample aliquots at 30 minute intervals.

All storm event samples were triggered based on a predicted minimum of 0.25 inches of precipitation. Sample collection dates are presented in Table 4; a total of 25 storm samples were collected from the tributaries, while 13 storm samples were collected from the two Green River main stem locations.

Table 4. Sample Collection Dates and Number of Samples Collected for Storm Event Conditions

Location	2011	2012								Total Count
	11/16	1/31	2/24	3/5	3/10	3/20	3/29	10/31	11/19	
Green River-Flaming Geyser		X	X	X	X	X	X[a]			7
Newaukum Creek		X	X	X	X	X			X	6
Soos Creek	X	X	X	X	X	X				6
Mill Creek	X	X			X	X	X	X		6
Black River	X	X		X		X	X	X[a]		7
Green River-Foster Links	X	X	X	X	X	X				6
Total Number of Storm Samples Collected										**38**

[a] Field replicate sample collected.

2.3.3 Evaluation of Sample Collection Methods

Evaluation of the autosampler collection method was conducted at the Green River – Foster Links location from the golf cart bridge within the Foster Links Golf Course. This evaluation was not conducted at the tributary locations as these water bodies are relatively small and well mixed; therefore, the opportunity for bias is less likely. Samples were collected on September 13 and December 3, 2012 to represent baseflow and storm event conditions, respectively. Samples were collected using two methods: (1) an ISCO® autosampler deployed in the same manner as described in Section 2.3.1 and 2.3.2; and (2) a Scott Bottle deployed at multiple locations over the cross-section of the river. Sample collection using both methods was initiated simultaneously.

The pre-cleaned Scott Bottle was deployed at approximately 2-3 meter intervals at 16 locations over the cross-section of the river. During the baseflow sampling event, maximum river depth was approximately 2 meters; however, depth in much of the cross-section ranged from 1.0-1.5 meters, with the exception of the very shallow east bank area that was not sampled. During baseflow conditions the Scott Bottle was deployed at mid-depth at each cross-section sample location. However, during the storm event sample collection the river depth was much greater, with a maximum depth of about 5.5 meters. At five of the 16 cross section locations, the Scott Bottle was deployed at multiple depths (1 and 4 meters below the water surface) to better capture the water quality conditions within the channel. A 500 ml sample aliquot was collected from each Scott Bottle cast and transferred to a 10-L pre-cleaned glass carboy. Three replicate samples were collected during each of the two sampling events.

The autosampler was deployed on the stream bank; the intake collection tubing was placed in the river channel approximately 6-8 feet from the bank. The intake tubing was placed at least 4-6 inches above the stream bottom by attaching it to a secure object (i.e., staff gage, fence post, railing, or cinder block). The autosampler was programmed to collect a 500 ml aliquot every 2-3 minutes. During both baseflow and storm event sampling, the autosampler was initially programmed to collect a sample aliquot at 3 minute intervals; however, the interval was changed to 2 minutes because the cross-section sampling effort

took less time than expected. Three replicate samples were collected during each of the two sampling events. The autosampler collected 17 (3 minute interval) or 18 (2 minute interval) sample aliquots per replicate.

Equipment blanks were not collected for this portion of the project. All samples were analyzed for total and dissolved arsenic, PAHs, TOC, DOC, and TSS; only one sample collected per method and event was analyzed for PCB congeners. A total of 12 samples were collected (Table 5).

Table 5. Sample Collection Dates and Number of Samples Collected for Sampling Methodology Evaluation

Sample Type	Number of Samples	
	Baseflow (9/13/2012)	Storm Event (12/3/2012)
Autosampler Composite (one location adjacent river bank)	3[a]	3[a]
Cross section Composite (multiple locations within river cross section)	3[a]	3[a]

[a] Only 1 sample analyzed for PCB congeners.

2.4 Sample Processing

As soon as possible following the completion of a sampling event, King County Field Science Unit (FSU) staff retrieved the sample carboys, and transported them on ice to the King County Environmental Laboratory (KCEL). The composite samples were then homogenized and transferred into the appropriate laboratory sample containers. 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.

One field equipment blank was collected at the KCEL on October 31, 2012. The field equipment blank is used to evaluate levels of contamination that might be associated with the sampling equipment and introduce bias into the sample result. An aliquot of a clean reference matrix (reverse osmosis water) was processed through the sampling equipment as a blank and analyzed for total and dissolved arsenic, PAHs, PCBs, TOC, DOC and TSS.

Samples for PCB congener analysis were delivered to AXYS Analytical Services (AXYS) within 1 to 4 months of sample collection. Samples were held at the KCEL at the appropriate temperature until delivery date. Samples were either driven to AXYS or shipped via overnight express delivery service.

2.5 Field Sampling Deviations from the SAP

All field sampling methods were conducted according to the SAP (King County 2011a) and the SAP addendum (King County 2012b) except where noted below.

- Section 2.2 of the SAP specified that storm event sampling at Newaukum, Soos and Mill creeks, would be triggered at a specific stage height above the estimated wet season baseflow stage. Trigger heights, which were above the estimated wet season baseflow stage, were intended such that a storm of approximately 0.25 to 0.5"rainfall in 12 hours (with a 24-hour antecedent dry period) should be sufficient to trigger sampling; however, less intense but longer duration storms could also initiate sampling. However, in practice, use of trigger heights to initiate sampling was not feasible. For example, at Soos and Newaukum creeks, rainfall events did not result in a large stage height increase, but rather an increase in velocity. In addition, trigger heights designated for Mill Creek presented in the SAP were later determined to have been based on Mill Creek in Kent rather than Auburn. Therefore, only predicted rainfall amounts of at least 0.25 inches were used to trigger storm sampling in these tributaries.
- Section 2.2 of the SAP describes the targeted storm event sampling conditions at the Black River Pump Station. The SAP specified that storm event samples were to be collected based on the number of pumps operating at the Pump Station. Unfortunately, pump operations were not predictable and it was not feasible to track the pumping schedule to anticipate specific flow conditions; during some sampling periods there was sporadic or limited pumping activity. The SAP also specified that storm event samples should be collected from the discharge of one of the series of nine pumps that regulate water release from the dam. As previously indicated pump operations were unpredictable and did not directly coincide with rain events. In responses to these challenges, the autosampler intake was placed just behind the dam near the Pump #1 intake to collect storm samples.
- Section 3.3 of the SAP specifies that the autosampler tubing and carboys would be decontaminated by rinsing with acetone, prior to each use. However, following collection of the baseflow samples it was determined that residual acetone in the tubing resulted in TOC and DOC concentrations that were biased high. As a result, baseflow data for these analytes were rejected (see Section 5.6.1). The biased data finding is based on testing of tubing equipment blanks. Based on this finding, the acetone rinse for both autosampler tubing and the carboy was eliminated for all storm event sample collection. The acetone rinse was intended to reduce the probability of PCB contamination between sampling events at a site. However, given the observed organic carbon bias due to residual acetone, AXYS Analytical agreed to this change. The remaining decontamination procedures for tubing and carboys were continued; therefore, this change was not expected to result in cross-contamination issues for storm event samples.

- Section 3.1 of the SAP specifies that autosamplers should be programmed to collect samples for a minimum of 12 hours and a maximum of 24 hours. However, at three locations the sample period exceeded 24 hours (Table 6), while at one location the sampling period was only 2 hours. While sampling periods exceeding 24 hours are not expected to affect the use of these data, samples collected within a 2 hour time span have the potential to be biased either low or high. The autosampler deployed at Mill Creek on 1/31/2012 was only operational for 2 hours. Flow in Mill Creek during this event was very high and the autosampler pulse rate was set too low to accommodate the elevated flow conditions; as a result, aliquots were collected every two minutes rather than every 30 to 60 minutes. Comparison of analytical data for this sample relative to other Mill Creek storm event samples indicated lower TSS concentrations; however, other parameters were within the range of those detected during other Mill Creek storm events.
- Section 3.7 of the SAP specifies that one field replicate will be collected at each location during the study. However, field replicates were only collected at two of the six locations (Black River and Green River - Flaming Geyser). At the Green River - Foster Links location, FSU staff attempted to collect a field replicate; however, an equipment failure prevented sample collection. Space limitations for securing sampling equipment at Newaukum, Soos, and Mill creeks prevented collection of replicates at these sites. Therefore, the focus of the overall sampling effort was to collect six storm events at each location and field replicates where possible.

Table 6. Sample Collection Events Outside of the 12-24 Hour Collection Period

Duration of Sampling Events Outside Defined 24 hr Period (Hrs)					
Location	Date - 2012				
	1/31	2/24	3/5	3/10	3/20
Mill Creek	2	-	-	30	-
Newaukum Creek	36	25	26	-	32
Soos Creek	25	-	-	-	-

3.0. LABORATORY METHODS

A summary of the laboratory analyses performed on all samples are 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 (LMCLs) and flagged down to the sample specific detection limit (SDL) value. In many cases the SDL may be below the LMCL. The following sections provide a summary of the laboratory methods; greater detail can be found in the study SAP (King County 2011a).

3.1 Arsenic

Total and dissolved arsenic samples were analyzed and reported by EPA Method 200.8 (Inductively Coupled Plasma-Mass Spectrometry [ICP-MS]), KCEL Standard Operating Procedure (SOP) 624.

3.2 Polycyclic Aromatic Hydrocarbons

PAHs samples were prepared by liquid-liquid extraction in general agreement with EPA method 3520C. Samples were analyzed by a modified EPA Method 8270 Gas Chromatography/Mass Spectrometry – Selected Ion Monitoring Large Volume Injection method (GC/MS-SIM LVI), developed for this study (see KCEL SOP 772v0). 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.

3.3 PCB Congeners

PCB congener analysis followed EPA Method 1668C Revision C (EPA 2010a), which is a high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) method using an isotope dilution internal standard quantification. The analysis included all 209 PCB congeners. AXYS performed the PCB congener analysis according to their SOP MLA-010.

On September 15, 2011, based on EPA's promulgation of a new method, AXYS changed from using Revision A of EPA Method 1668 (EPA 2003) to Revision C of this method (EPA 2010a). Method 1668C provides reliable analyte identification and very low detection limits. Both versions of this method add an extensive suite of labeled surrogate standards before sample extraction. Data are "recovery-corrected" for losses in extraction and clean-

up, and analytes are quantified against their labeled analogues. The principle difference between Method 1668A and 1668C is the replacement of individual laboratory acceptance criteria with inter-laboratory developed acceptance criteria.

3.4 Conventional Water Quality Parameters

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

3.5 Analytical Deviations from the SAP

All analytical laboratory methods followed those described in the SAP with the following exception:

- Section 4.2 of the SAP specified that for PAH analysis, 1 liter samples would be extracted and concentrated to a final volume of 1.0 ml. While the first seven samples were extracted in one workgroup with a final volume of 1.0 ml, the matrix was clean enough that the final volume was adjusted to 0.5 ml for all other samples to maximize the number of detections.

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. The analytical results presented in report tables represent the precision of the analytical laboratory for each parameter.

4.1 Summation for PAHs and PCB Congeners

For most PAH data analyses, PAHs were summed as low molecular weight PAHs (LPAHs) and high molecular weight PAHs (HPAHs) following the definitions set under the Washington State Sediment Management Standards (Ecology 1995). 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.

For total LPAHs and HPAHs and total PCBs, only detected concentrations of individual PAHs or PCB congeners were included in their respective totals. However, in some instances, no PAH compounds were detected in a sample. When this occurred, the single highest U-flagged value for an individual PAH compound was used to represent the total LPAH or HPAH and flagged as a non-detect result.

4.2 Laboratory and Field Replicates

Laboratory replicates were considered laboratory quality control values and were not used in data analysis, but rather as part of the data validation process. 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 higher of two U-flagged values was used. This was often the MDL value.
- When one result was detected and one was a non-detect, the combined value was the average of the detected value and ½ the U-flagged value.
- When both results were detected, the two concentrations were simply averaged.

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

4.3 Data Analysis Methods

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

The two main stem Green River locations are influenced by dam releases and represent much larger drainage areas relative to the tributaries evaluated here. As a result, the hydrodynamics and source inputs associated with these systems are expected to be different. Based on these differing conditions, comparison of baseflow to storm event conditions were evaluated separately for main stem Green River sites and the tributaries. The Black River was also evaluated separately from the other tributaries because the Pump Station creates unique hydrological conditions (see Section 2.1). Combining the two Green River main stem locations and combining the three tributary locations, allowed for higher statistical power in the analysis due to the increased number of samples.

For comparisons of baseflow to storm event conditions, T-tests were conducted using Sigma Plot 12.0 software. 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. These statistical tests were also used to explore differences in concentrations for all parameters between the upstream and downstream main stem sampling locations (Green River – Flaming Geyser and Green River – Foster Links). Parametric t-tests can identify statistical differences in means between two groups, while the Rank Sum tests can identify differences in medians. Unless otherwise noted, t-tests concluding no statistical difference had statistical power of greater than 0.80.

Comparison of storm event concentrations for all parameters across all sites were analyzed using one-way analysis of variance (ANOVA), followed by the Holm-Sidak method for pairwise multiple comparison ($p<0.05$). Baseflow concentrations were not included in the analysis because of low sample size ($N = 3$ per location). The ANOVAs were performed with Sigma Plot 12.0 software. If the data did not pass the Shapiro-Wilk Normality test ($p<0.05$) or the Equal Variance test ($p<0.05$), then the non-parametric Kruskal-Wallis ANOVA on Ranks was performed ($p<0.05$), followed the Tukey Test procedure for pairwise multiple comparison ($p<0.05$). Figures in Section 7.0 have significant differences labelled.

In addition, correlation analysis was conducted to examine relationships between chemical and physical parameters; the findings of this analysis are presented in Section 5.8. Correlation analyses were performed with Sigma Plot 12.0 software. Normality was determined using the Shapiro-Wilk Normality test ($p<0.05$). Pearson Product Moment Correlation analysis was used for normally distributed data while Spearman Rank-Order Correlation tests were used for non-parametric data ($p< 0.05$). Data for the Green River main stem sites were combined for correlation analysis as were three of the tributaries (Newaukum, Soos, and Mill creeks). The Black River was not included in the tributary analysis due to the unique flow conditions at this location (see Section 2.1). Baseflow data were not included in the correlation analysis because of the smaller number of samples, especially compared to the storm event dataset. Although the storm event dataset was used, sample-sizes were still fairly limited. Different correlation results could be observed if an even larger dataset were available.

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 field 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 and data correlation analyses are presented in Section 5.8.

5.1 Conventional Parameters

This section summarizes the conventional water quality parameters results. As discussed in Section 5.6, results for TOC and DOC analyses in baseflow samples are not included due to data quality issues that resulted in high bias. The cause of the TOC and DOC data quality issues was discovered and addressed prior to collection of the storm event samples (see Section 2.5); therefore, all TOC and DOC results for storm event samples are presented below.

5.1.1 Total Organic Carbon

TOC concentrations measured during storm event conditions are summarized in Table 7. Mean storm event TOC concentrations ranged from 2.40 mg/L at the Green River – Flaming Geyser location to 9.69 mg/L in Mill Creek. The highest TOC concentration was detected in Newaukum Creek (18.8 mg/L). In general, median storm event TOC concentrations were similar to mean concentrations. Storm event concentrations at both Green River locations were lower than most concentrations in the tributary locations (Figure 4). Figure 5 presents TOC concentrations by collection date and location.

Table 7. Summary of Storm Event TOC and DOC (mg/L) Data by Site.

Site	Parameter (mg/L)	Flow	FOD	Min	Max	Mean	Median
Green River – Flaming Geyser	TOC	Storm	6/6	1.48	4.73	2.40	1.93
	DOC		6/6	1.31	4.62	2.18	1.70
Newaukum Creek	TOC	Storm	6/6	4.69	18.8	8.73	7.57
	DOC		6/6	4.42	14.8	7.60	6.76
Soos Creek	TOC	Storm	6/6	3.91	8.44	5.43	4.85
	DOC		6/6	3.71	7.06	4.84	4.34
Mill Creek	TOC	Storm	6/6	8.68	10.7	9.69	9.61
	DOC		6/6	7.16	9.75	8.59	8.74
Black River	TOC	Storm	6/6	6.00	9.45	6.97	6.58
	DOC		6/6	4.97	8.68	6.23	5.67
Green River - Foster Links	TOC	Storm	6/6	2.68	7.01	3.84	3.29
	DOC		6/6	2.40	5.73	3.13	2.46

FOD – Frequency of detection.

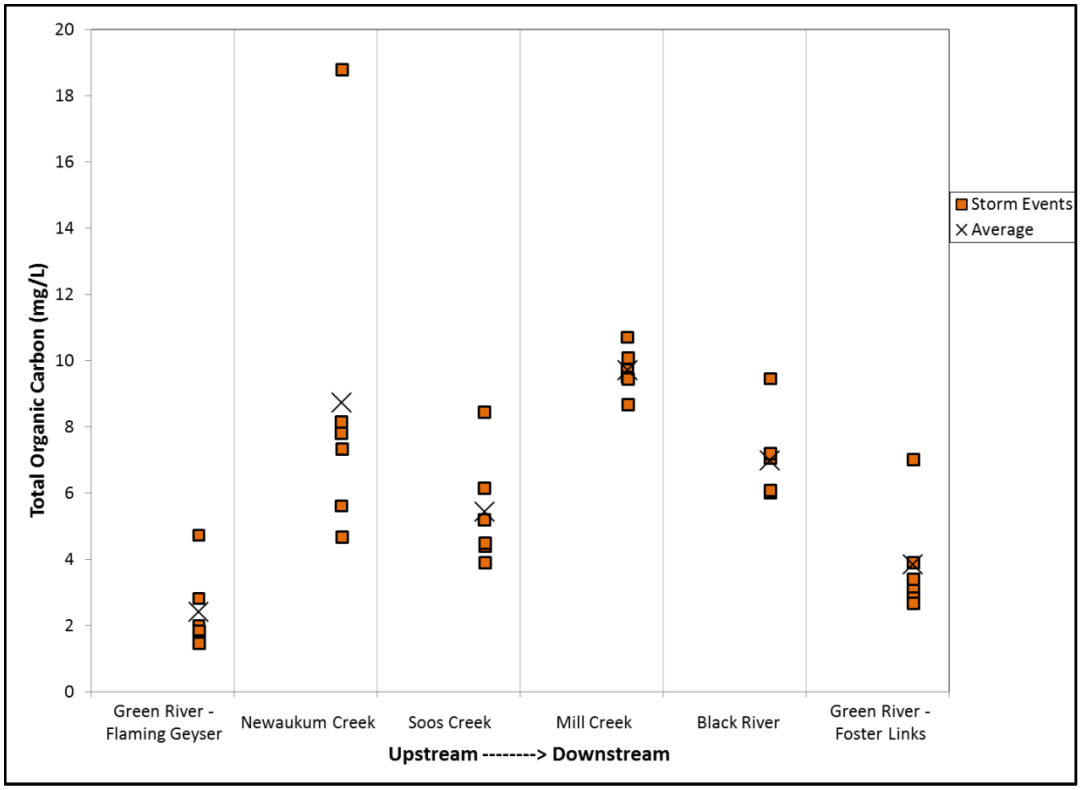


Figure 4. TOC by Site and Flow Condition

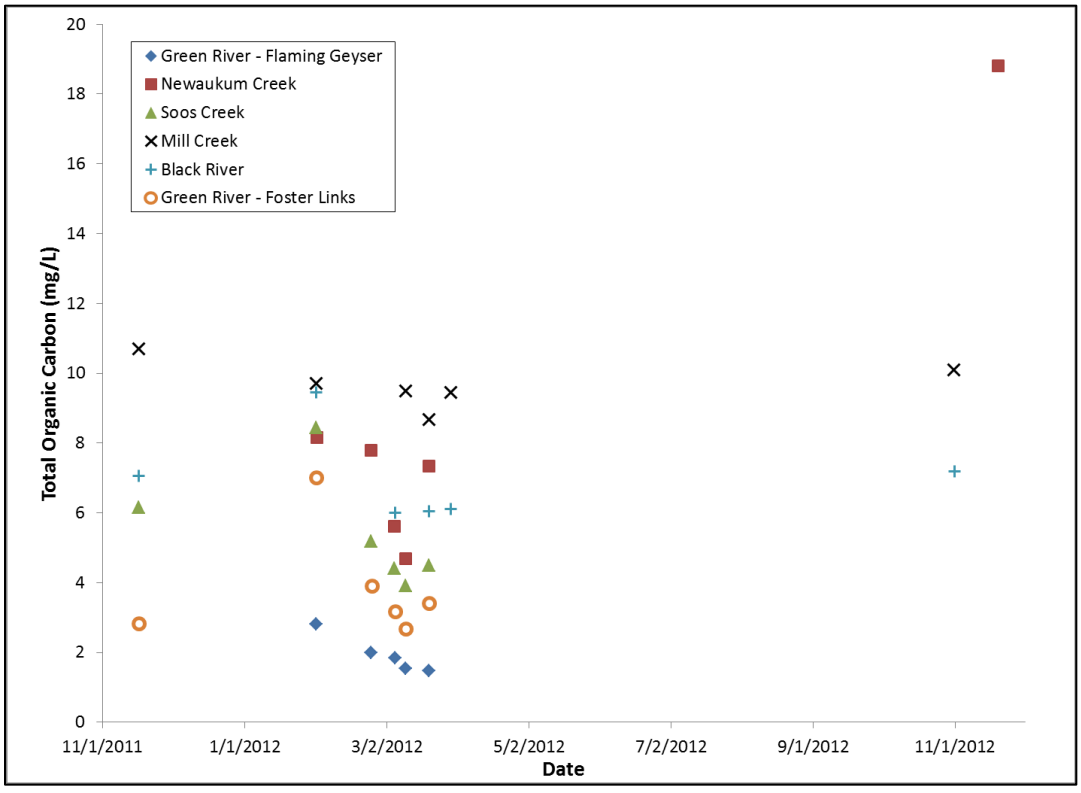


Figure 5. TOC by Sample Collection Date

5.1.2 Dissolved Organic Carbon

DOC concentrations measured in storm event samples are summarized in Table 7. Mean DOC concentrations during storm events ranged from 2.18 mg/L at the Green River – Flaming Geyser location to 8.59 mg/L in Mill Creek. The highest DOC concentration was detected in Newaukum Creek (14.8 mg/L). In general, median storm event DOC concentrations were similar to mean concentrations. As observed with TOC, most storm event DOC concentrations at both Green River locations were lower than levels measured in the tributaries (Figure 6). Figure 7 presents DOC concentrations by collection date and location.

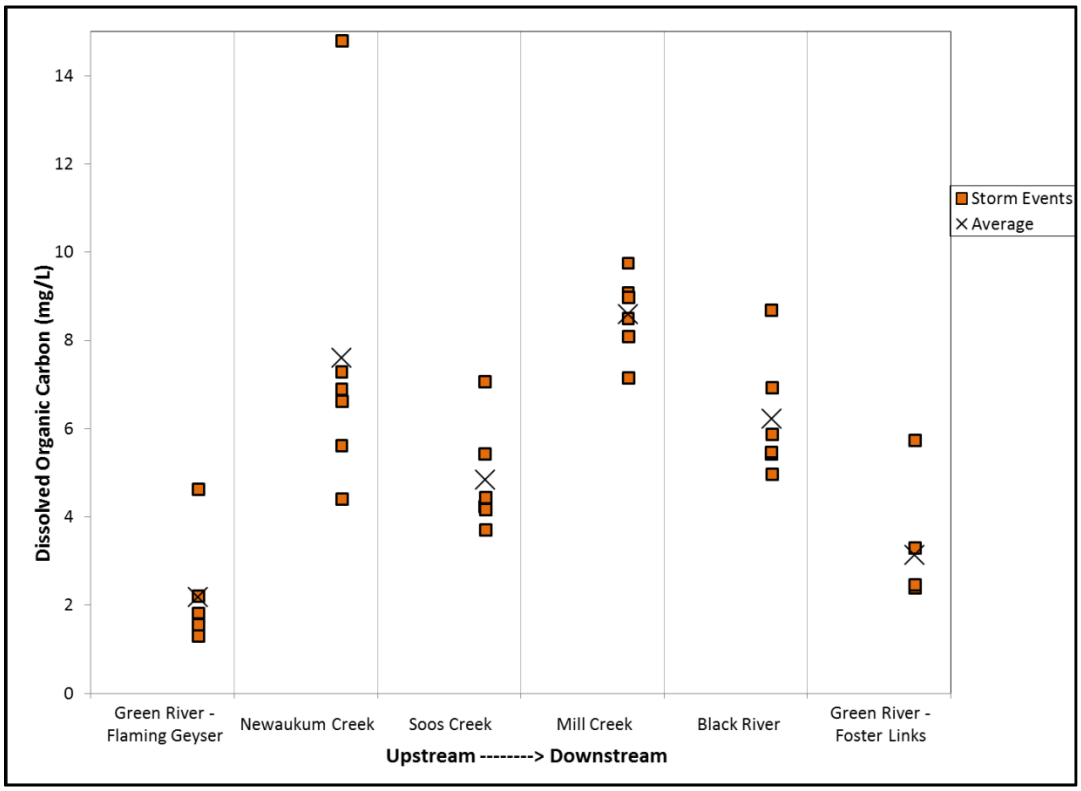


Figure 6. DOC by Site and Flow Condition

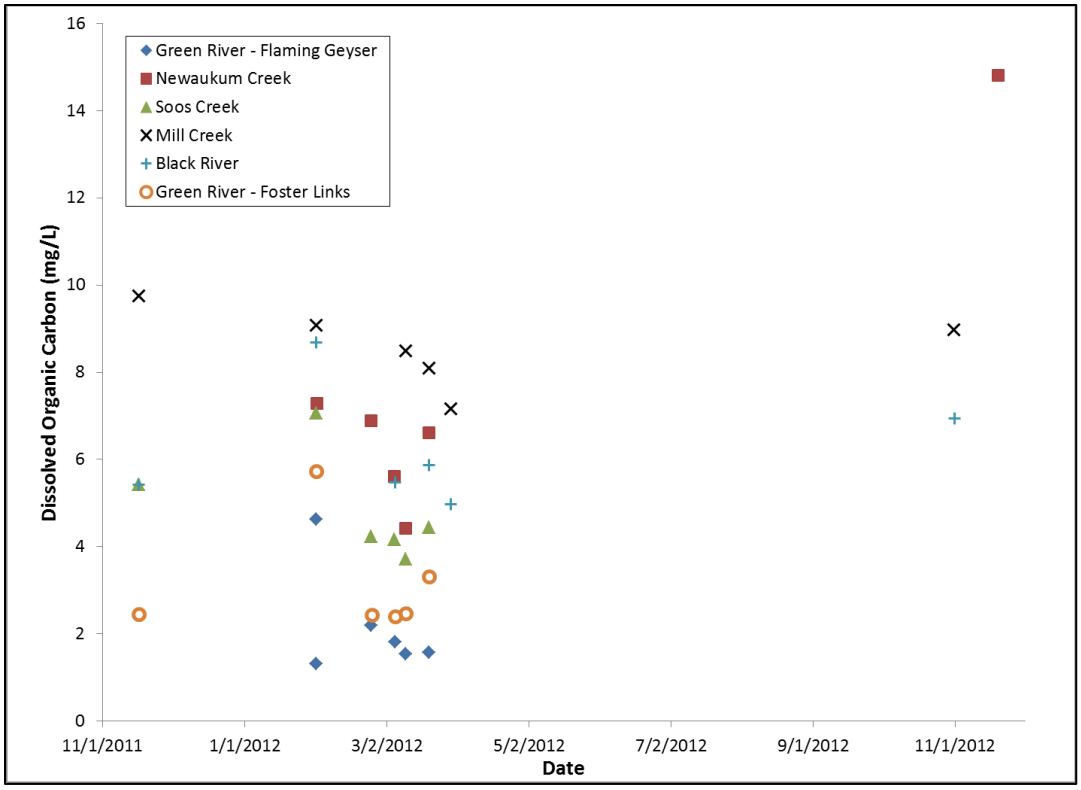


Figure 7. DOC by Sample Collection Date

5.1.3 Total Suspended Solids

TSS concentrations in both baseflow and storm event samples are summarized in Table 8. During baseflow conditions, mean TSS concentrations were generally similar across location and ranged from 1.78 mg/L in Newaukum Creek to 4.36 mg/L in the Black River. Mean TSS concentrations in storm event samples were higher than levels in baseflow samples and ranged from 6.09 mg/L in the Black River to 34.0 mg/L at the Green River – Foster Links location. The highest single TSS concentration in storm event samples was detected at the Green River – Foster Links location (102 mg/L). Median and mean baseflow concentrations were relatively similar at all locations. Median storm event concentrations were lower than mean storm concentrations at all locations except the Black River. With the exception of the Black River where TSS concentrations in baseflow and storm event samples were similar, TSS concentrations were usually higher in storm event samples (Figure 8). However, TSS concentrations in four of the storm event samples collected from the Green River – Flaming Geyser location were similar to concentrations in baseflow samples. The greatest variability in TSS was observed at the Green River - Foster Links location followed by Mill Creek (Figure 8). Figure 9 presents TSS concentrations by collection date and location.

Table 8. Summary of TSS (mg/L) Data by Site and Flow Condition

Site	Flow	FOD	Min	Max	Mean	Median
Green River – Flaming Geyser	Base	3/3	1.62	2.47	2.02	1.96
	Storm	6/6	1.30	52.8	12.2	2.21
Newaukum Creek	Base	3/3	1.65	1.90	1.78	1.80
	Storm	6/6	3.20	43.6	11.3	4.22
Soos Creek	Base	3/3	2.40	2.71	2.57	2.60
	Storm	6/6	4.00	18.4	7.48	5.82
Mill Creek	Base	3/3	3.78	4.40	3.99	3.78
	Storm	6/6	7.20	66.4	24.8	14.7
Black River	Base	3/3	4.20	4.63	4.36	4.24
	Storm	6/6	4.60	7.78	6.09	5.86
Green River - Foster Links	Base	3/3	2.89	4.95	3.93	3.96
	Storm	6/6	6.90	102	34.0	16.9

FOD – Frequency of detection.

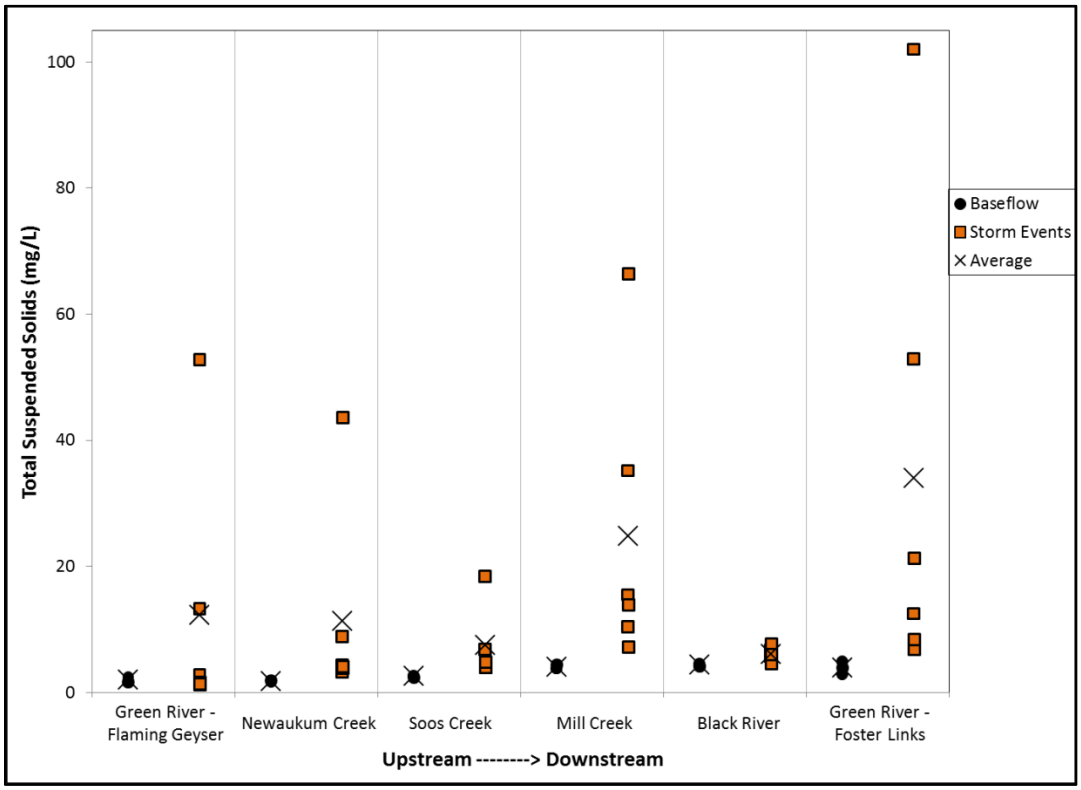


Figure 8. TSS by Site and Flow Condition

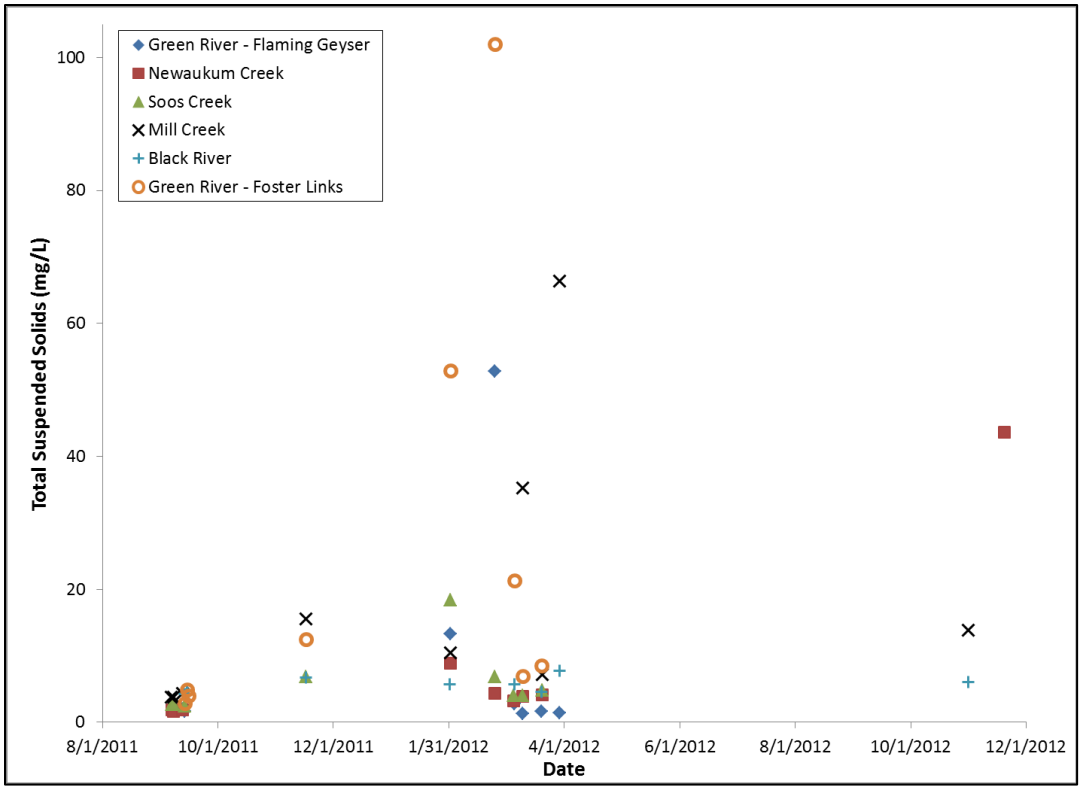


Figure 9. TSS by Sample Collection Date

5.2 Arsenic

Arsenic (total and dissolved) was detected in all samples; results are summarized separately for total and dissolved arsenic in the following sections.

5.2.1 Total Arsenic

A summary of total arsenic concentrations measured in both baseflow and storm event samples are presented in Table 9. During baseflow conditions, mean total arsenic concentrations ranged from 0.647 µg/L in Newaukum Creek to 1.05 µg/L in Soos Creek. Mean total arsenic concentrations during storm events ranged from 0.50 µg/L in Newaukum Creek to 1.05 µg/L in Mill Creek; the highest single concentration of total arsenic was detected at the Green River – Foster Links location (1.71 µg/L). During both baseflow and storm event conditions, mean and median total arsenic concentrations were similar at all locations with the exception of storm event samples collected from Mill Creek and the Green River-Foster Links location, where mean concentrations were slightly higher than median concentrations (Table 9).

At the three most upstream sites (Green River – Flaming Geyser, Newaukum and Soos creeks), mean total arsenic concentrations under baseflow conditions were higher than those detected during storm events (Table 9). When individual data from the three most upstream sites are compared, almost all sample results show total arsenic concentrations

lower during storm events than baseflow conditions (Figure 10). Mean total arsenic concentrations were similar during both baseflow conditions and storm events at the Green River – Foster Links location and the Black River, while levels are slightly higher during storm events than baseflow conditions in Mill Creek. In general, storm event concentrations were more variable than baseflow levels (Figure 10). Figure 11 presents total arsenic concentrations by collection date for each location.

Table 9. Summary of Total and Dissolved Arsenic (µg/L) Data by Site and Flow Condition

Site	Arsenic	Flow	FOD	Min	Max	Mean	Median
Green River – Flaming Geyser	Total	Base	3/3	0.765	0.871	0.804	0.775
		Storm	6/6	0.42 J	0.848	0.54 J	0.50 J
	Dissolved	Base	3/3	0.787	0.809	0.797	0.795
		Storm	6/6	0.30 J	0.511	0.42 J	0.43 J
Newaukum Creek	Total	Base	3/3	0.625	0.668	0.647	0.648
		Storm	6/6	0.42 J	0.668	0.50 J	0.48 J
	Dissolved	Base	3/3	0.636	0.651	0.641	0.636
		Storm	6/6	0.41 J	0.622	0.47 J	0.45 J
Soos Creek	Total	Base	3/3	0.998	1.08	1.05	1.08
		Storm	6/6	0.539	0.934	0.682	0.644
	Dissolved	Base	3/3	0.973	1.04	1.00	0.987
		Storm	6/6	0.47 J	0.777	0.58 J	0.541
Mill Creek	Total	Base	3/3	0.781	0.814	0.802	0.810
		Storm	6/6	0.855	1.48	1.05	0.887
	Dissolved	Base	3/3	0.704	0.733	0.714	0.706
		Storm	6/6	0.504	0.864	0.676	0.658
Black River	Total	Base	3/3	0.814	0.862	0.838	0.838
		Storm	6/6	0.760	0.974	0.868	0.845
	Dissolved	Base	3/3	0.47 J	0.501	0.49 J	0.49 J
		Storm	6/6	0.49 J	0.739	0.60 J	0.587
Green River – Foster Links	Total	Base	3/3	0.916	1.04	0.966	0.941
		Storm	6/6	0.591	1.71	0.964	0.794
	Dissolved	Base	3/3	0.692	0.728	0.709	0.706
		Storm	6/6	0.37 J	0.47 J	0.43 J	0.43 J

FOD – Frequency of detection; J – Value estimated.

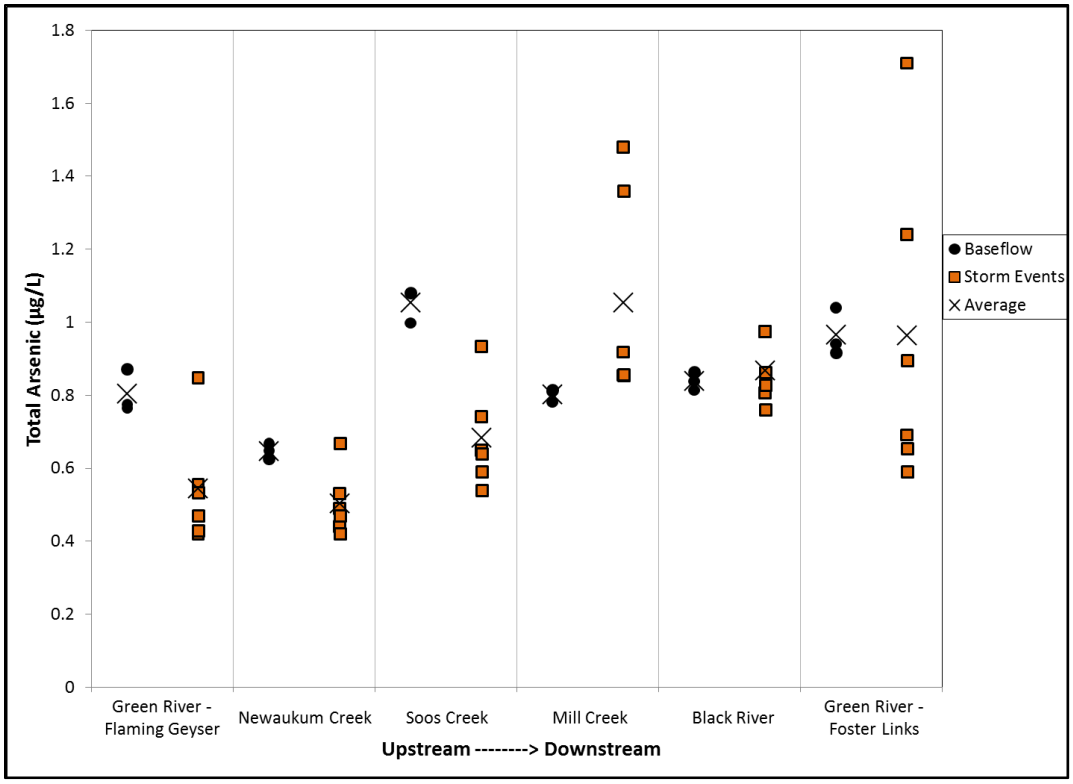


Figure 10. Total Arsenic by Site and Flow Condition

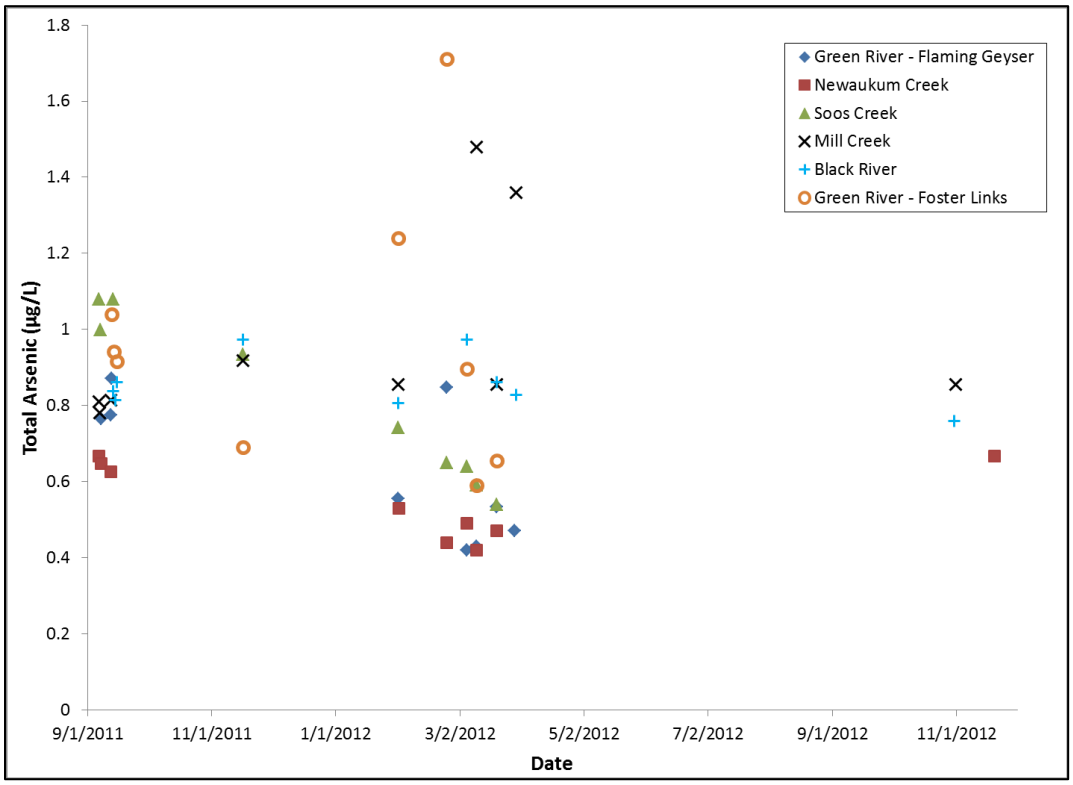


Figure 11. Total Arsenic by Sample Collection Date

5.2.2 Dissolved Arsenic

A summary of dissolved arsenic concentrations measured during both baseflow and storm event conditions are presented in Table 9. Mean dissolved arsenic concentrations during baseflow conditions ranged from 0.49 µg/L in the Black River to 1.00 µg/L in Soos Creek. During storm events, mean dissolved arsenic ranged from 0.42 µg/l at the Green River - Flaming Geyser location to 0.676 µg/l in Mill Creek. Mean and median dissolved arsenic concentrations were similar at all locations (Table 9).

With the exception of the Black River, mean dissolved arsenic concentrations were generally higher during baseflow conditions than during storm events. However, in Mill Creek, baseflow concentrations of dissolved arsenic fall within the range of those measured during storm events (Figure 12); baseflow concentrations in the Black River also overlapped with concentrations measured during two storm events. Figure 13 presents total arsenic concentrations by collection date for each location.

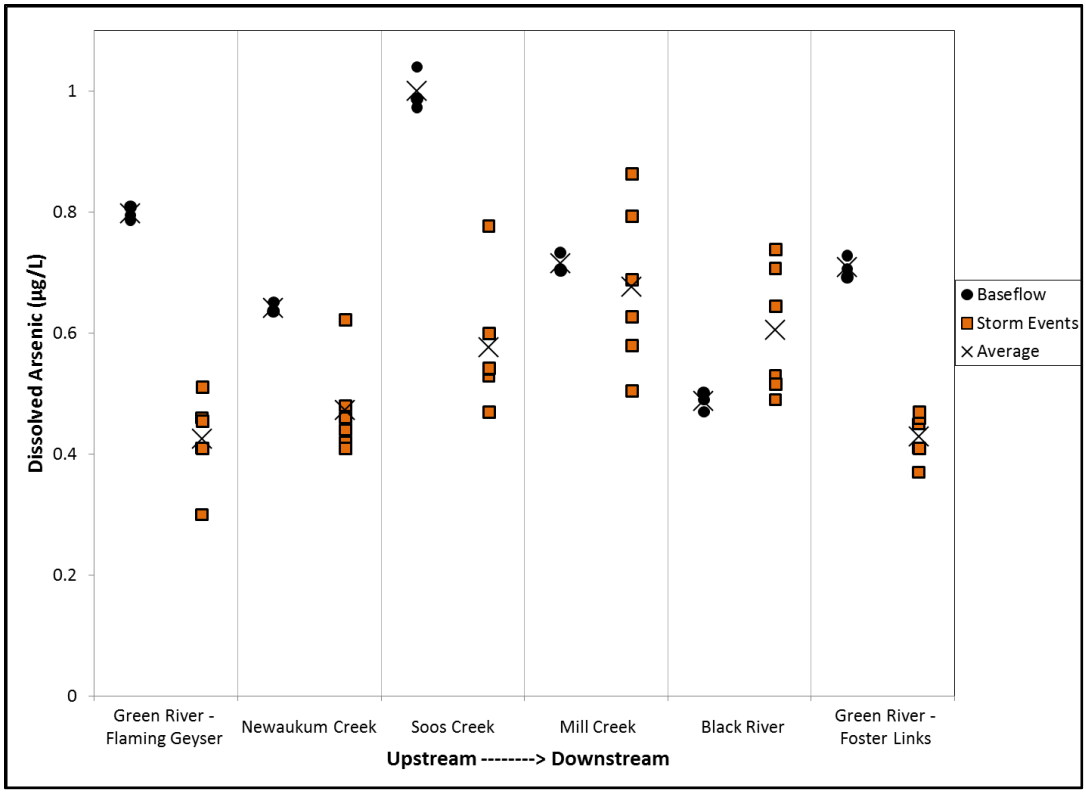


Figure 12. Dissolved Arsenic by Site and Flow Condition

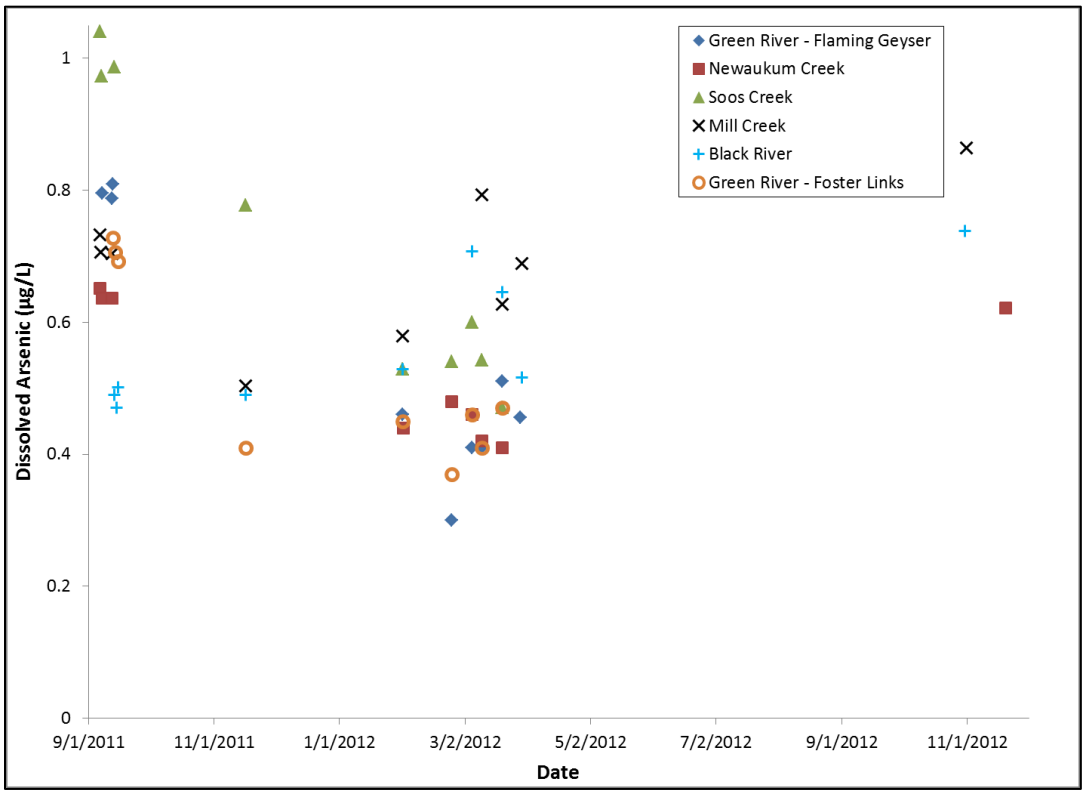


Figure 13. Dissolved Arsenic by Sample Collection Date

5.3 PAHs

PAH data are summarized as individual LPAH and HPAH compounds in tabular format for frequency of detection and graphical format for maximum detections. Total LPAHs and HPAHs are presented in tabular and graphical format. These data are discussed in the following sections.

5.3.1 LPAHs

The number of individual LPAHs detected in each sample was highly variable. With the exception of phenanthrene, which was never detected, all individual LPAHs were detected in at least one sample (Table 10). Individual LPAHs were detected more frequently during storm events than under baseflow conditions. The greatest number of individual PAHs was detected in the Black River, while the fewest individual PAHs were detected in the Green River –Flaming Geyser location. MDLs ranged from 0.00014 to 0.00095 µg/L depending on the PAH compound (see Appendix B). For most LPAH compounds, the highest detected concentrations during storm events were generally observed in the Black River. At all locations, naphthalene concentrations were highest of all individual LPAH compounds detected. Figure 14 illustrates maximum detected concentration of individual LPAHs by site and flow condition.

Table 10. Frequency of Detection for Individual LPAH Compounds by Site and Flow Condition

LPAH Compound	Green River - Flaming Geyser		Newaukum Creek		Soos Creek		Mill Creek		Black River		Green River - Foster Links	
	Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm
Acenaphthene	1/3	1/6	2/3	2/6	3/3	2/6	2/3	1/6	3/3	5/6	3/3	2/6
Acenaphthylene	2/3	1/6	0/3	4/6	3/3	6/6	3/3	5/6	3/3	6/6	3/3	4/6
Anthracene	0/3	0/6	0/3	3/6	0/3	6/6	2/3	6/6	3/3	6/6	1/3	6/6
Fluorene	1/3	1/6	2/3	2/6	2/3	2/6	2/3	1/6	3/3	4/6	0/3	2/6
Naphthalene	1/3	5/6	1/3	3/6	3/3	3/6	1/3	5/6	1/3	5/6	2/3	4/6
Phenanthrene	0/3	0/6	0/3	0/6	0/3	0/6	0/3	0/6	0/3	0/6	0/3	0/6

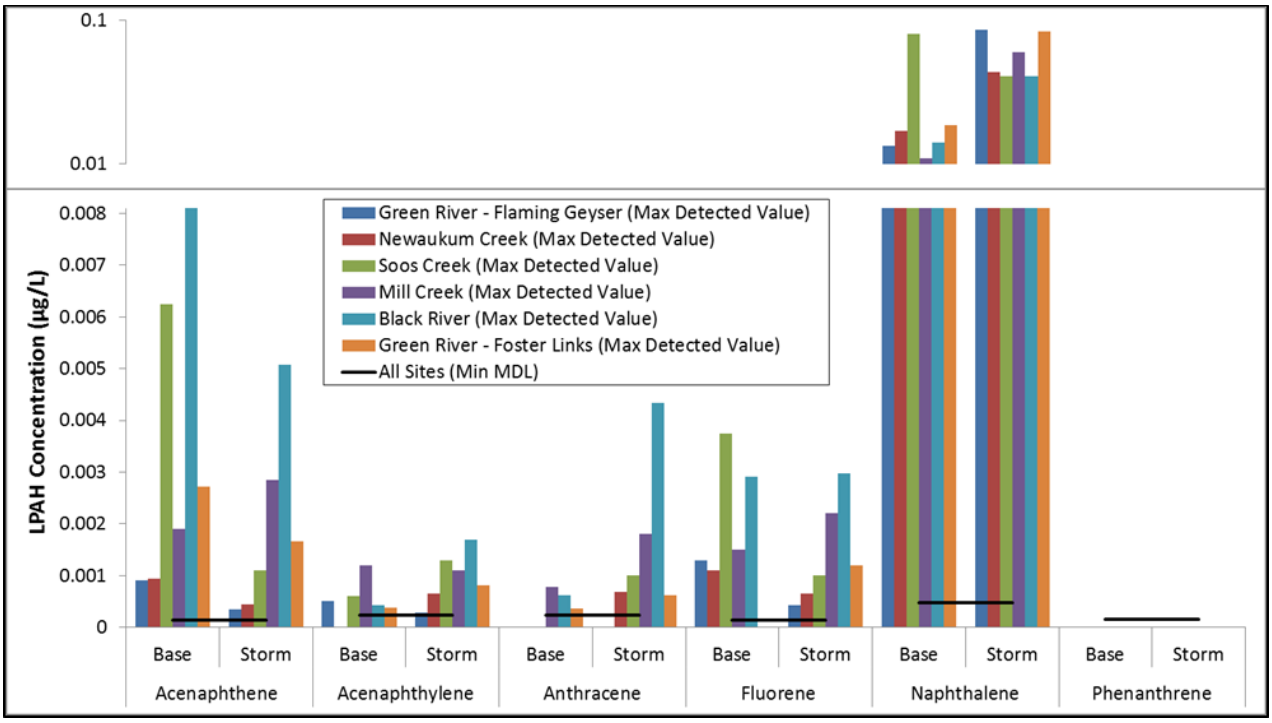


Figure 14. Maximum Detected Concentration of Individual LPAH Compounds by Site and Flow Condition

A summary of total LPAH concentrations is presented in Table 11. Under baseflow conditions, mean LPAH concentrations ranged from 0.0082 µg/L in Mill Creek to 0.0535 µg/L in Soos Creek. The highest overall LPAH concentration was detected under baseflow conditions in Soos Creek (0.101 µg/L). Mean storm event LPAH concentrations ranged from 0.0244 µg/L in Newaukum Creek to 0.051 µg/L in Mill Creek. In general, median storm event LPAH concentrations were similar to, or slightly lower than, the mean concentrations. With the exception of the Green River –Foster Links location, a similar pattern was observed under baseflow conditions at all locations (the median was not calculated for the Green River – Flaming Geyser location because LPAH compounds were only detected in two of the three baseflow samples).

In general, LPAH concentrations were variable under both baseflow and storm event conditions at all locations (Figure 15). This variability is in part, likely related to the low frequency of detection and low detected concentrations; relatively small differences in concentration can appear as relatively high variability between samples. With the exception of Soos Creek, mean storm event concentrations were higher than those observed during baseflow conditions; however, baseflow concentrations fall within the range of those detected in storm event samples for all locations (Figure 15). Figure 16 summarizes total LPAH concentrations by collection date for each location.

Table 11. Summary of Total LPAHs (µg/L) Data by Site and Flow Condition

Site	Flow	FOD	Min	Max	Mean[a]	Median[a]
Green River – Flaming Geyser	Base	2/3	0.00025 J	0.0238 J	0.010 J	n/c
	Storm	5/6	0.0212 J	0.0945 J	0.0475 J	0.0473 J
Newaukum Creek	Base	3/3	0.00193 J	0.0308	0.0116 J	0.00204 J
	Storm	5/6	0.00069 J	0.0688 J	0.024 J	0.0125 J
Soos Creek	Base	3/3	0.0163 J	0.101 J	0.0535 J	0.0435 J
	Storm	6/6	0.00099 J	0.0663 J	0.030 J	0.0244 J
Mill Creek	Base	3/3	0.0042 J	0.0150 J	0.00820 J	0.00538 J
	Storm	6/6	0.00708 J	0.0821 J	0.0512 J	0.0537 J
Black River	Base	3/3	0.0111 J	0.0347 J	0.0192 J	0.0118 J
	Storm	6/6	0.00516 J	0.0728 J	0.0368 J	0.0374 J
Green River – Foster Links	Base	3/3	0.00287 J	0.0375 J	0.0253 J	0.0356 J
	Storm	6/6	0.00036 J	0.0941 J	0.034 J	0.0235 J

[a] Mean and median concentrations were calculated with detected concentrations and the MDL for non-detect results. Total LPAHs represent the sum of detected individual PAH concentrations. If no individual LPAHs were detected in a given sample, the highest non-detect value (U-flagged) was used.

FOD – Frequency of detection; n/d – Non-detect; n/c – Not calculated if FOD less than 3/6.
J – Value estimated.

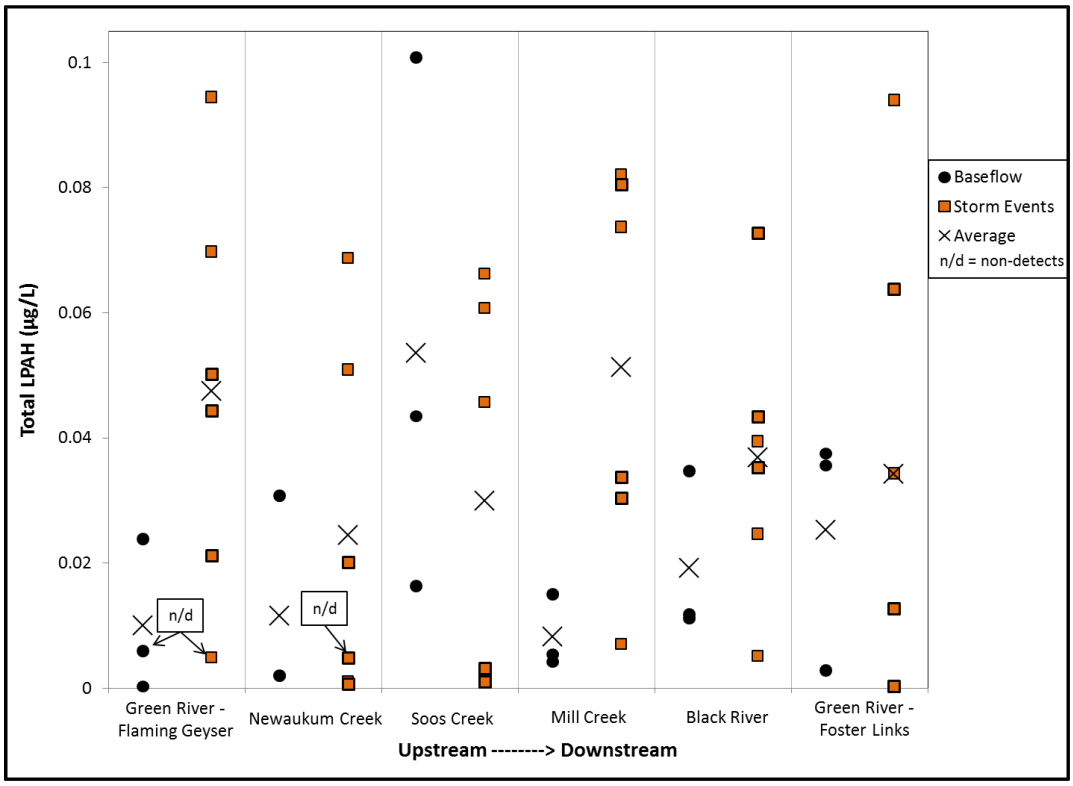


Figure 15. Total LPAHs by Site and Flow Condition

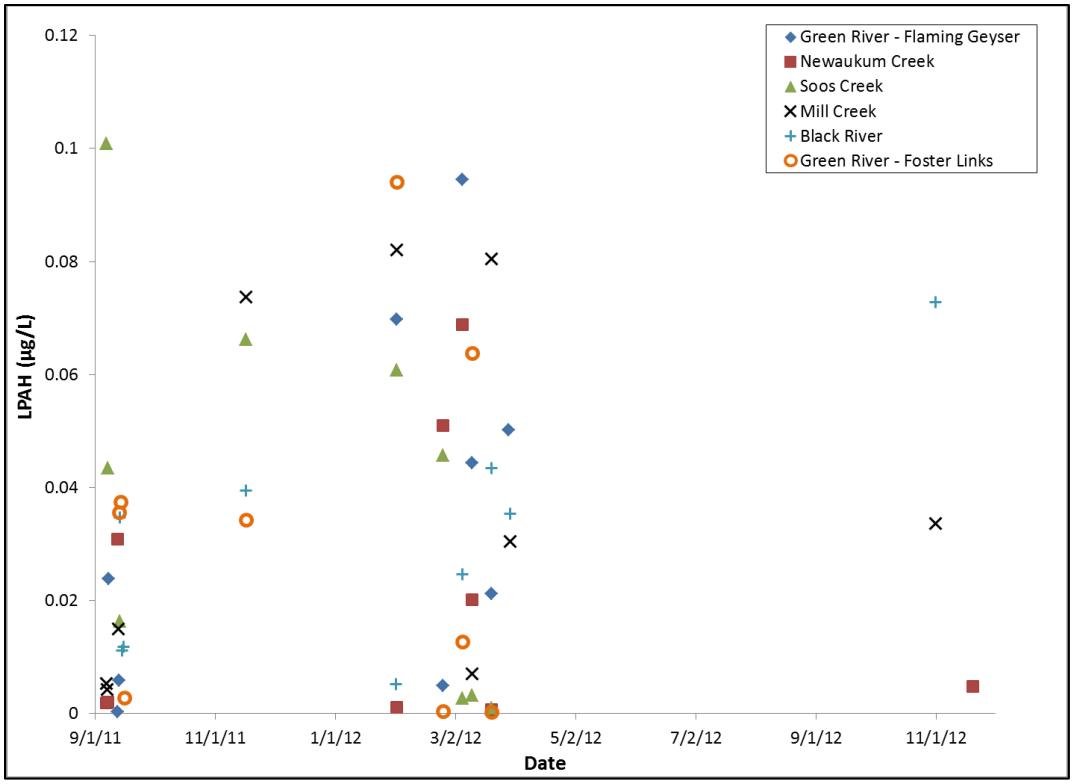


Figure 16. Total LPAHs by Sample Collection Date

5.3.2 HPAHs

All individual HPAHs were detected in at least one sample. The number of individual HPAHs detected in each sample was variable; however, the frequency of detection was low in most samples (Table 12). Individual HPAHs were detected more frequently in storm event samples than in baseflow samples. The greatest number of individual HPAHs was detected in the Black River, while the least number of detections was found in the Green River –Flaming Geyser location. MDLs ranged from 0.00016 to 0.00095 µg/L depending on the PAH compound (see Appendix B). For all HPAH compounds, the highest detected concentrations were observed in the Black River. Figure 17 illustrates maximum detected concentration of individual HPAHs by site and flow condition.

Table 12. Frequency of Detection for Individual HPAH Compounds by Site and Flow Condition

HPAH Compound	Green River - Flaming Geyser		Newaukum Creek		Soos Creek		Mill Creek		Black River		Green River - Foster Links	
	Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm
Benzo(a)-anthracene	0/3	0/6	0/3	1/6	0/3	2/6	0/3	6/6	3/3	6/6	0/3	5/6
Benzo(a)pyrene	0/3	0/6	0/3	1/6	0/3	0/6	0/3	6/6	2/3	6/6	0/3	5/6
Benzo(b,j,k)-fluoranthene	0/3	0/6	0/3	4/6	0/3	3/6	1/3	6/6	3/3	6/6	1/3	6/6
Benzo(g,h,i)-perylene	0/3	1/6	0/3	1/6	0/3	2/6	1/3	6/6	3/3	6/6	0/3	6/6
Chrysene	0/3	2/6	0/3	4/6	0/3	6/6	2/3	6/6	3/3	6/6	1/3	6/6
Dibenzo(a,h)-anthrancene	0/3	0/6	0/3	0/6	0/3	0/6	0/3	1/6	0/3	6/6	0/3	1/6
Fluoranthene	0/3	0/6	0/3	0/6	0/3	0/6	0/3	1/6	0/3	6/6	0/3	1/6
Indeno(1,2,3-Cd)-pyrene	0/3	1/6	0/3	1/6	0/3	2/6	1/3	6/6	2/3	6/6	0/3	6/6
Pyrene	0/3	0/6	0/3	0/6	0/3	0/6	0/3	3/6	3/3	6/6	0/3	1/6

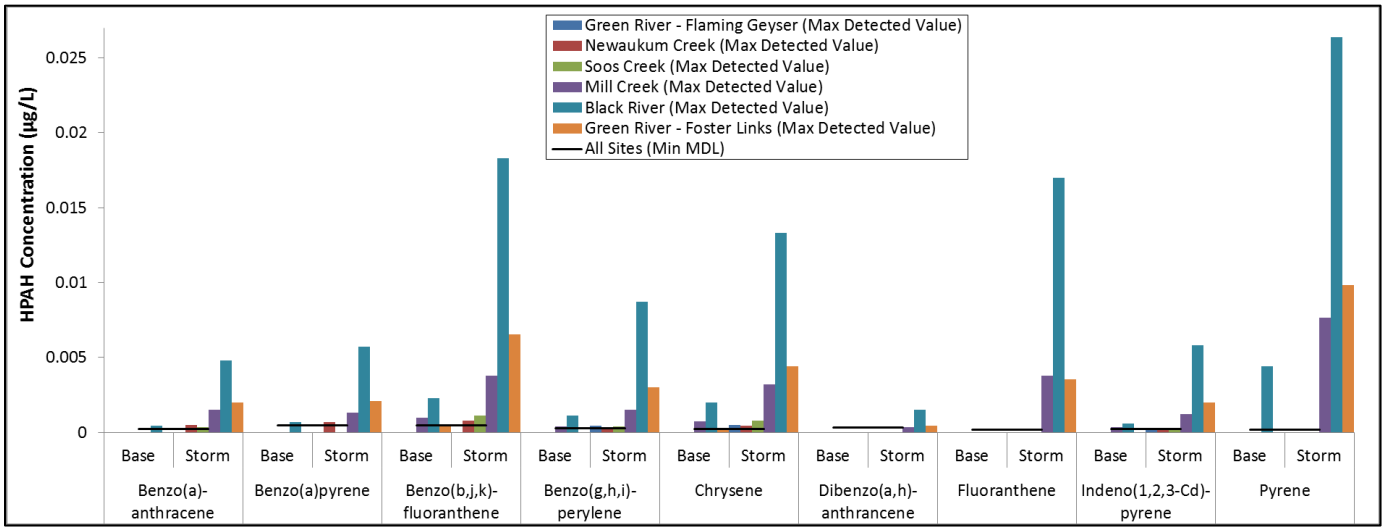


Figure 17. Maximum Detected Concentration of Individual HPAH Compounds by Site and Flow Condition

Total HPAH concentrations in both baseflow and storm event samples are summarized in Table 13. During baseflow conditions, HPAHs were not detected in samples from the three most upstream sites (Green River – Flaming Geyser, Newaukum and Soos creeks). The highest mean HPAH concentration during baseflow conditions was detected in the Black River (0.0101 µg/L); this concentration is about an order of magnitude greater than the mean concentrations at Mill Creek and the Green River-Foster Links location. HPAHs were detected in most storm event samples. The highest mean HPAH concentration in a storm event sample was detected in the Black River (0.065 µg/L). Mean storm event concentrations in the Black River, Mill Creek and Green River-Foster Links location were at least an order of magnitude higher than mean concentrations in the Green River-Flaming Geyser location, and Newaukum and Soos creeks. In general, median storm event HPAH concentrations were similar to mean concentrations except at the Green River-Foster Links location and Mill Creek where median concentrations were lower (Table 13).

All HPAH concentrations during storm events were higher than those during baseflow conditions in Mill Creek, the Black River and the Green River-Foster Links location (Figure 18). While HPAHs were not detected in baseflow samples from the Green River-Flaming Geyser location and Newaukum and Soos creeks, at least one HPAH was detected in most storm event samples collected from Newaukum and Soos creeks. Figure 19 presents total HPAH concentrations by collection date and location.

Table 13. Summary of Total HPAHs (µg/L) Data by Site and Flow Condition

Site	Flow	FOD	Min	Max	Mean[a]	Median[a]
Green River – Flaming Geyser	Base	0/3	n/d	n/d	0.0021 U	n/c
	Storm	2/6	0.00029 J	0.00121 J	0.0014J	n/c
Newaukum Creek	Base	0/3	n/d	n/d	0.0026 U	n/c
	Storm	5/6	0.00090 J	0.00165 J	0.0013 J	0.00122 J
Soos Creek	Base	0/3	n/d	n/d	0.0027 U	n/c
	Storm	6/6	0.00035 J	0.0022 J	0.0012 J	0.0011 J
Mill Creek	Base	2/3	0.00052 J	0.0025 J	0.0021 J	n/c
	Storm	6/6	0.00556 J	0.0191 J	0.0115 J	0.0106 J
Black River	Base	3/3	0.0094 J	0.0109 J	0.0101 J	0.0100 J
	Storm	6/6	0.0388 J	0.102 J	0.0651 J	0.0656 J
Green River – Foster Links	Base	1/3	n/d	0.00076 J	0.0013 J	n/c
	Storm	6/6	0.00377 J	0.0303 J	0.0110 J	0.00775 J

[a] Mean and median concentrations were calculated with detected concentrations and the MDL for non-detect results. Total HPAHs represent the sum of detected individual PAH concentrations. If no individual HPAHs were detected in a given sample, the highest non-detect value (U-flagged) was used.

FOD – Frequency of detection; n/d – Non-detect; n/c – Not calculated if FOD less than 3/6; J – Value estimated

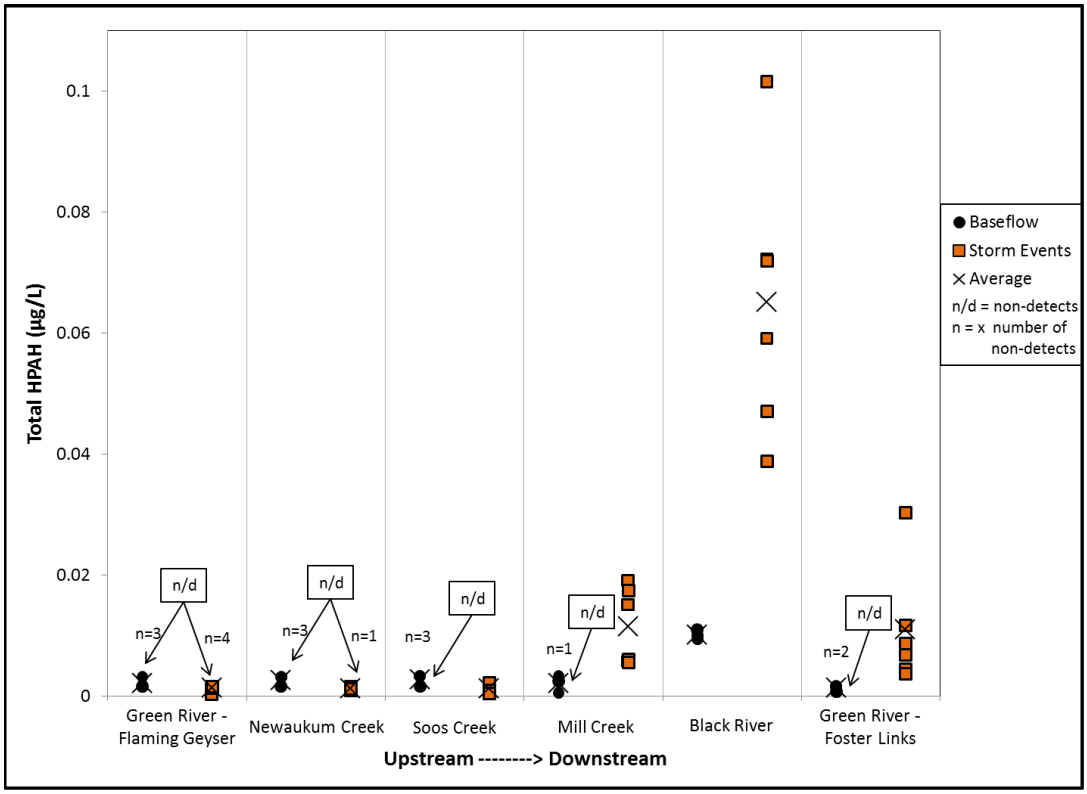


Figure 18. Total HPAHs by Site and Flow Condition

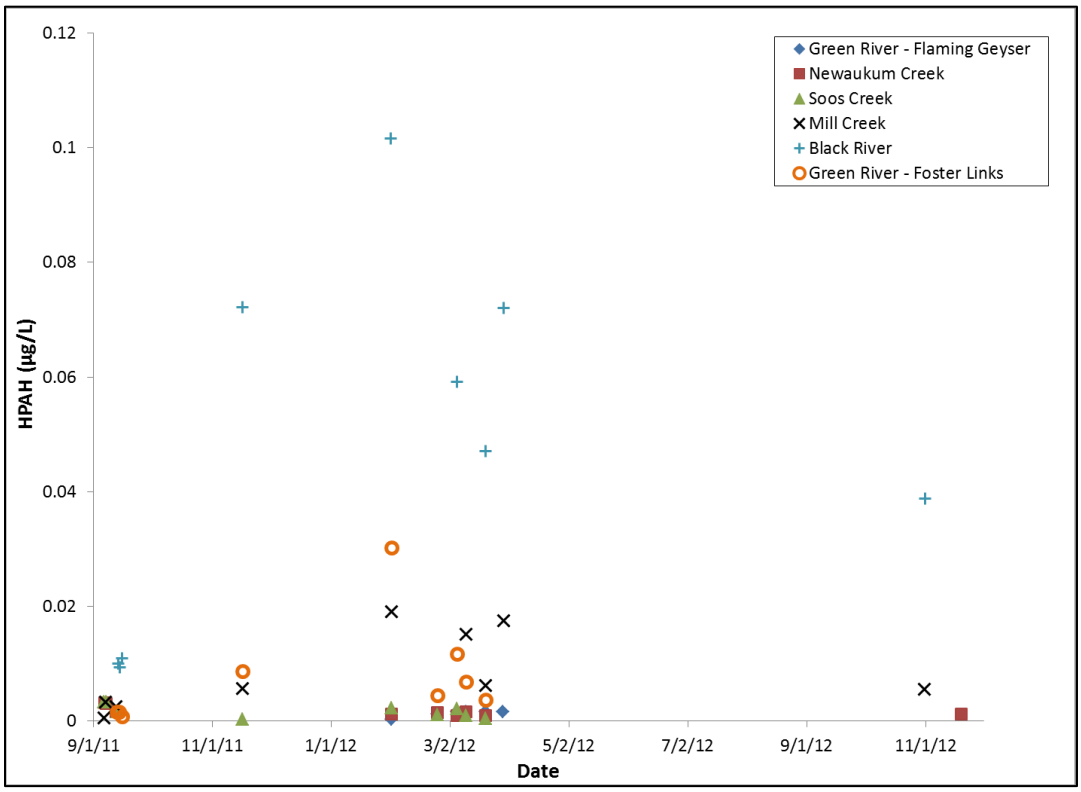


Figure 19. Total HPAHs by Sample Collection Date

5.4 Total PCBs

Total PCB concentrations during both baseflow and storm event conditions are summarized in Table 14[6]. PCBs were detected in all baseflow and storm event samples. During baseflow conditions, mean total PCB concentrations ranged from 79.8 pg/L at the Green River – Flaming Geyser location to 1,590 pg/L in Soos Creek. During baseflow conditions, the highest single total PCB concentration was detected in Soos Creek (4,680 pg/L). All other total PCB baseflow concentrations were about an order of magnitude or less than this concentration. For example, the second highest baseflow concentration of 452 pg/L was measured in Newaukum Creek. Mean total PCB concentrations in storm event samples ranged from 84.1 pg/L at the Green River – Flaming Geyser location to 940 pg/L in the Black River. Median storm event concentrations were lower than mean storm concentrations at all sampling locations. Under baseflow conditions, median concentrations were also lower than mean concentrations at all locations except Mill Creek and the Green River - Foster Links location, but concentrations were similar. The greatest difference between baseflow concentrations was observed at Soos Creek where the total PCBs in one sample were over 100 times higher than the next highest baseflow concentration. With the exception of Soos and Newaukum creeks, mean storm event total PCB concentrations at all locations were similar or higher than those during baseflow conditions. However, baseflow concentrations generally fall within the range of levels detected during storm events (Figure 20). Figure 21 presents total PCB concentrations by collection date and location.

Table 14. Summary of Total PCB (pg/L) Data by Site and Flow Condition

Site	Flow	FOD	Min	Max	Mean	Median
Green River – Flaming Geyser	Base	3/3	37.8 J	142 J	79.8 J	59.4 J
	Storm	6/6	23.0 J	171 J	84.1 J	80.6 J
Newaukum Creek	Base	3/3	35.4 J	452 J	177 J	45.3 J
	Storm	6/6	39.1 J	205 J	87.8 J	72.4 J
Soos Creek	Base	3/3	41.4 J	4,680 J	1,590 J	45.0 J
	Storm	6/6	36.2 J	160 J	93.3 J	88.4 J
Mill Creek	Base	3/3	91.0 J	121 J	110 J	118 J
	Storm	6/6	72.2 J	486 J	278 J	223 J
Black River	Base	3/3	137 J	423 J	261 J	222 J
	Storm	6/6	319 J	2133 J	940 J	756 J
Green River – Foster Links	Base	3/3	56.3 J	106 J	84.9 J	92.8 J
	Storm	6/6	74.4 J	316 J	161 J	119 J

FOD – Frequency of detection; J – Value estimated.

[6] 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.

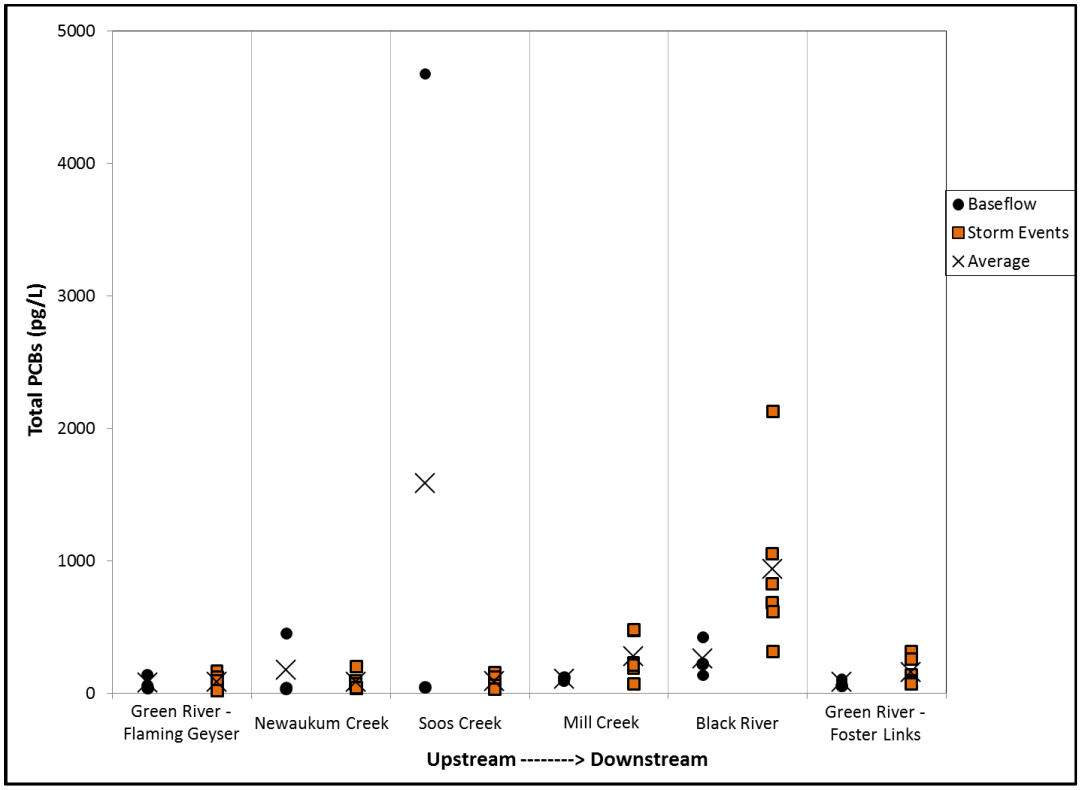


Figure 20. Total PCBs by Site and Flow Condition

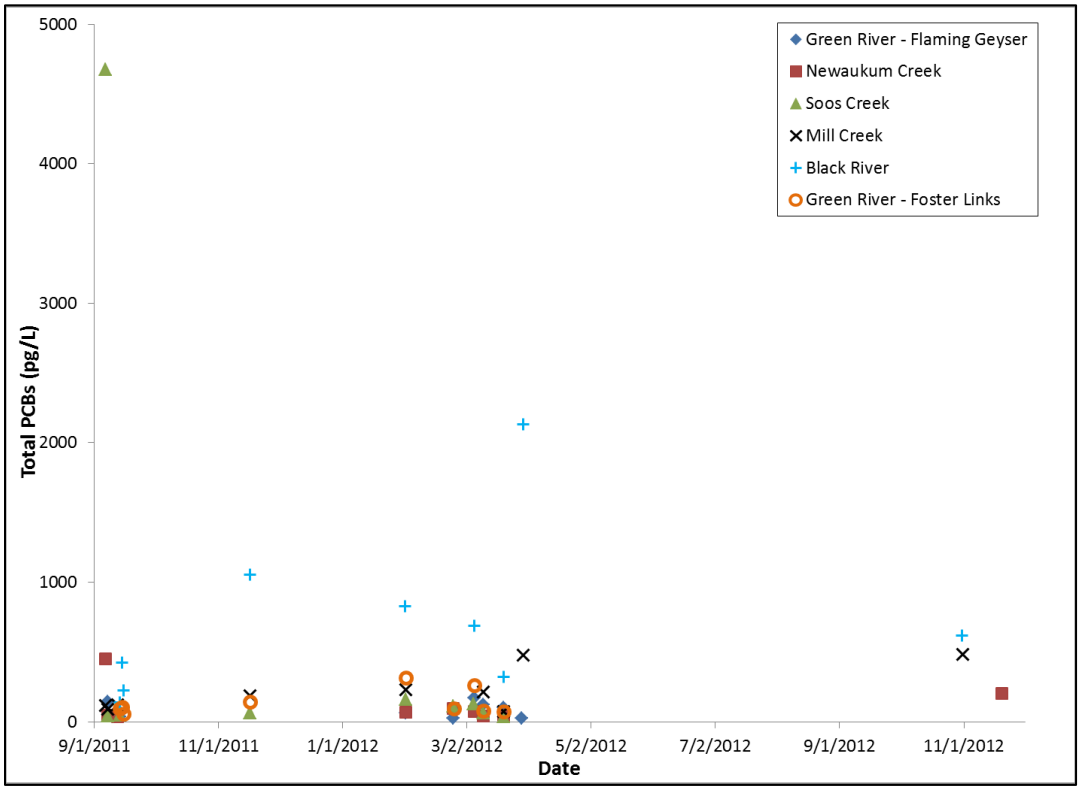


Figure 21. Total PCBs by Sample Collection Date

5.5 Quality Control/ Quality Assurance Samples

This section presents the results for field 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 Field Blank

Field blank samples provide an indication of potential chemical contamination associated with field equipment. They can help detect false positives or biased high results by identifying if chemical contamination is associated with sampling and storage equipment. Table 15 presents the field blank results. Arsenic, HPAHs and TSS were not detected in these samples; LPAHs were detected at very low levels. The same LPAH compounds detected in the field blank were also detected in laboratory method blank samples.

Total PCBs in the single field blank sample were at 155 pg/L. PCBs were also detected in laboratory method blank samples at concentrations ranging from 33 to 91 pg/L. The laboratory method blank associated with the field blank sample had a total PCB concentration of 33 pg/L. For another King County study (King County 2013b) the KCEL reverse-osmosis water, which is used for field blanks in this study, was analyzed for PCB congeners and had a total PCB concentration of 31.8 pg/L. When analyzing PCBs at such low detection levels, it is not uncommon to detect low levels of PCB contamination in laboratory method blanks. However, the field 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 field blank include the congeners indicative of contamination from silicone tubing (i.e., PCB-47, PCB-51, and PCB-68); these comprised approximately 70% of the total PCBs. The remaining PCB total is similar to that observed in laboratory water used to generate the field blank. The field 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 the silicone tubing used in sample collection and processing (Section 1.0).

TOC and DOC were detected at low levels in the field blank. These levels were similar to minimum concentrations detected at the Green River Flaming Geyser location. While only one field blank sample was analyzed, these results suggest a potential bias to samples; however, for most sample results the bias is not likely to be significant.

Table 15. Summary of Field Blank Results

Dissolved Arsenic	Total Arsenic	Total HPAHs	Total LPAHs	Total PCBs	TOC	DOC	TSS
µg/L				pg/L	mg/L		
n/d (0.1)	n/d (0.1)	n/d (0.00047)[a]	0.0434 J	155[b] J	1.14	1.03	n/d (0.5)

n/d – Non-detect; Method Detection Limit (MDL) in parentheses; J - Value estimated.

[a] Represents the highest MDL for individual HPAH compound.

[b] Coeluting congener groups PCB-44/47/65. PCB-45/51, and PCB-68 comprised 108 pg/L of this total.

5.5.2 Field Replicates

Field replicate samples provide an indication of natural and analytical variability. As previously discussed, two field replicates (Green River – Flaming Geyser and Black River) were collected over the course of the sampling period. Table 16 summarizes the comparison of the field replicate samples.

Table 16. Comparison of field replicate results

Parameter	Green River – Flaming Geyser			Black River		
	Sample	Replicate	RPD	Sample	Replicate	RPD
Total As (µg/L)	0.47 J	0.47 J	0%	0.770	0.750	3%
Dissolved As (µg/L)	0.45 J	0.46 J	2%	0.742	0.735	1%
LPAHs (µg/L)	0.0560	0.0444	23%	0.117 J	0.0285 J	122%
HPAHs (µg/L)	0.0017 U	0.0017 U	0%	0.0396 J	0.0380 J	4%
Total PCBs (pg/L)	34.0 J	12.0 J	96%	656 J	582 J	12%
TOC (mg/L)	1.51	1.45	4%	7.50	6.89	8%
DOC (mg/L)	1.24	1.38	11%	7.00	6.88	2%
TSS (mg/L)	1.24	1.65	28%	6.00	6.02	0%

RPD – Relative percent difference; U – Non-detect; J - Value estimated.

The relative percent differences (RPDs) between parameter concentrations in field replicates were variable. The greatest differences were observed for LPAHs in the Black River (RPD = 122 %). With the exception of LPAHs in the Black River and total PCBs and TSS at the Green River - Flaming Geyser location, RPDs for field replicate samples were below the required RPD for laboratory duplicate samples as described in the SAP (King County 2011a). The relatively high RPD for LPAHs in the Black River samples is driven by a higher detected concentration of naphthalene in the replicate sample. Total PCBs in the Green River – Flaming Geyser samples were very low, which influenced the RPD result. Overall, there were very few PCB congener detections in either sample, and those that were detected were flagged as estimates. The RPD for TSS of 28% in the Green River - Flaming Geyser location replicate is just above the laboratory duplicate requirement of 25%. With the exception of LPAHs in one field replicate pair, the field replicates indicate relatively low variability between the primary sample and field replicate. However, this is based on a limited number of field replicates at only two sampling locations.

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 the study SAP. Details of this validation are described in a data validation technical memorandum (Appendix C). Validation of PCB congener data was completed by Laboratory Data Consultants, Inc. (LDC) in accordance with EPA Superfund guidance (EPA 2009). 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 Unit 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 and, therefore, many analytes did not require qualifiers. However, some analytes were qualified with a J, indicating an estimated value. Data validation resulted in rejecting the TOC and DOC baseflow samples for the reasons discussed below. All analytical data except those rejected are of acceptable quality based on the data validation findings. Issues that resulted in the qualification of data are summarized below.

The analytical method for dissolved arsenic requires that samples be filtered within the method-specified 15 minute-holding time. Due to the 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.

The initial version of the SAP specified that all sample tubing and collection carboys be decontaminated by rinsing with acetone prior to each use. Following collection of the baseflow samples, it was determined that the TOC and DOC analyses were biased high as a result of residual acetone in the silicon tubing. When equipment blanks were tested, it was determined that the acetone was the cause of false positives in the TOC and DOC analyses. As a result, the TOC and DOC data for the baseflow samples were rejected (R qualified) by the data validator. None of the TOC and DOC analyses in storm event samples were impacted because the acetone rinse was discontinued prior to their collection. Following this finding, the SAP was updated to reflect the change in decontamination procedures.

Between 5 and 12 PAH compounds were detected in each method blank associated with the data presented in this report. All PAH method blank results were detected at concentrations less than the reporting detection limit (RDL), which is the limit of practical quantitation. Therefore, current EPA guidance (EPA 2008) rules were applied by the validator and results where the sample concentration was greater than the RDL and greater than 10 times the method blank concentration remained unqualified. When the detected method blank and sample concentrations were less than the RDL, the sample result was changed to the numeric RDL value and received a "U" validation qualifier. When method blank concentrations were detected and less that the RDL and the sample concentration was greater than the RDL, but less than 10 times the method blank concentration, the sample result remained as reported but received a "U" validation qualifier. Sample results were treated as not detected when "U" validation qualifiers are applied.

Individual PAH compounds in multiple samples were qualified for one of the following reasons: spike blank recoveries and RPDs were outside of QC limits, laboratory duplicates

exceeded QC limits, and in some cases, matrix spike recovery limits were not met. Samples were qualified with a "J" flag and considered estimated with either low or high bias. The most frequently qualified PAH was naphthalene, which was "J" flagged in 28 storm event samples because of high RPDs in laboratory duplicates.

5.6.2 PCBs

PCB data were validated to Level III by LDC. 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 and a few samples experienced sample-sample duplicate relative significant differences outside of method specifications. These method deviations resulted in some congener detections being flagged as estimated (J qualified).

PCBs were detected in all method blank samples. One or more mono- or di-chlorinated PCB congener were detected in the method blanks. Several method blanks had detections across the entire PCB homolog range. Between 17 and 33 PCB congeners were detected in the methods blanks. The total PCBs detected in method blanks ranged from 33.9 to 91.2 pg/L. Environmental sample detections were qualified as non-detect by the contract validator whenever congener concentrations were less than five times the method blank concentration. 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.

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 by the validator as non-detects (U qualified) according to the 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

As previously discussed, precipitation and flow data were collected during each sampling event. This section presents precipitation and flow data associated with the sampling periods.

5.7.1 Precipitation

Precipitation data are summarized (as total inches) in Table 17 including precipitation measurements for both the sampling period and the 12 hours preceding initiation of the

sampling event. Precipitation occurring prior to sample initiation may influence flow conditions during sample collection. Baseflow samples were collected during the dry season; therefore, precipitation is only reported for storm event sampling periods. With the exception of one event at Mill Creek (1/31/2012), total precipitation exceeded 0.25 inches of rainfall (Table 17). The rainfall totals for Mill Creek on 1/31/2012 are much lower than other locations sampled on this day because the sampler collected samples for less than 2 hours rather than the 12 hour minimum. As previously noted in Section 2.3.2, flow in Mill Creek during this event was elevated and the autosampler pulse rate resulted in sample aliquots being collected every two minutes rather than every 30 to 60 minutes.

Table 17. Summary of Precipitation and Flow Data for each Sampled Storm Event

Site	Date	Sampling Duration (hours)	Total Precipitation During Sample Collection and 12 Hours Before (inches)[a]	Flow (cfs)[b]		
				Min	Max	Mean
Green River – Flaming Geyser	1/31/2012	17	0.50	2,380	2,950	2,805
	2/24/2012	24	0.43	5,320	6,760	5,988
	3/5/2012	24	0.26	1,480	1,600	1,573
	3/10/2012	24	0.54	1,100	1,110	1,105
	3/20/2012	24	0.58	965	1,210	1,144
	3/29/2012	24	1.05	980	1,700	1,141
Newaukum Creek	1/31/2012	35	0.50	164	223	192
	2/24/2012	25	0.43	120	146	134
	3/5/2012	26	0.26	62	75	73
	3/10/2012	23	0.54	49	62	51
	3/20/2012	32	0.58	122	151	137
	11/19/2012	17	1.57	136	214	183
Soos Creek	11/16/2011	22	0.43	57	70	62
	1/31/2012	25	0.58	521	558	545
	2/24/2012	22	0.50	311	345	326
	3/5/2012	16	0.34	216	228	224
	3/10/2012	18	0.37	184	210	194
	3/20/2012	23	0.52	362	377	368
Mill Creek	11/16/2011	22	0.57	22[d]	28[d]	25[d]
	1/31/2012	1.3	0.04[c]	14[d]	14[d]	14[d]
	3/10/2012	30	0.78	16	30	19
	3/20/2012	13	0.22[c]	40	42	41
	3/29/2012	20	1.01	27	48	39
	10/31/2012	5	0.32	78	81	80
Black River	11/16/2011	24	0.45	n/a	n/a	n/a
	1/31/2012	24	0.50	n/a	n/a	n/a

Site	Date	Sampling Duration (hours)	Total Precipitation During Sample Collection and 12 Hours Before (inches)[a]	Flow (cfs)[b]		
				Min	Max	Mean
	3/5/2012	23	0.28	n/a	n/a	n/a
	3/20/2012	24	0.35	n/a	n/a	n/a
	3/29/2012	24	1.08	n/a	n/a	n/a
	10/31/2012	22	0.68	n/a	n/a	n/a
Green River – Foster Links	11/16/2011	24	0.45	981	1,590	1,182
	1/31/2012	18[e]	0.50	4,380	4,590	4,439
	2/24/2012	24	0.39	7,140	8,660	7,830
	3/5/2012	21	0.28	2,250	2,380	2,323
	3/10/2012	24	0.73	1,640	1,750	1,675
	3/20/2012	24	0.35	1940[f]	2280[f]	2,041[f]

[a] Section 2.3 lists rainfall gages used for each sample location.

[b] Section 2.2 presents flow gages or flow measurement methods for each sample location.

[c] Total precipitation less than 0.25.

[d] Flow estimated from upstream gage because ISCO® flow meter was damaged during high flow event.

[e] Sample duration estimated.

[f] Flow data only available for portion of sampling event; no data for 3/21/2012.

5.7.2 Flow

The minimum, maximum, and mean flow (cfs) during each sampled storm event is presented in Table 17. As presented in Section 2.2, flow data for Soos and Newaukum creeks and the two Green River locations were based on USGS gages. The USGS gaging stations used to estimate flow at the two Green River sites are located below Howard Hanson Dam for the Green River Flaming Geyser location and at Auburn for the Green River Foster Links location. Flow in Mill Creek was estimated using an ISCO® flow meter deployed during storm events; flow during baseflow sample collection was measured with a Swoffer hand held flow meter. As previously discussed in Section 2, flow at the Black River Pump Station could not be measured.

During sampled storm events, mean estimated flow at the Green River - Flaming Geyser location ranged from 1,105 to 5,988 cfs and from 1,182 to 7,830 cfs for the Green River - Foster Links location. Only two sampling events at the main stem Green River locations corresponded with significant (>2000 cfs at USGS gaging station below the Dam) dam releases (1/31/2012 and 2/24/2012). Of the tributaries, Soos Creek generally experienced the highest flow during storm events, followed by Newaukum and Mill creeks; Mill Creek experienced some of the lowest flow conditions. Relative to Soos and Newaukum creeks, Mill Creek is relatively small in both basin size (see Table 1) and stream width where samples collected (a bank full width of approximately 15 feet).

Flow conditions during collection of baseflow samples are summarized in Table 18. Base flows in the main stem Green River were approximately 300 cfs, while flow in the tributaries ranged from 27 cfs in Soos Creek to about 1 cfs in Mill Creek. Baseflow at Black

River Pump Station is based on pumping rate at the fish ladder, where samples were collected.

Table 18. Mean Flow (cfs) During Baseflow Sampling Events

Site	Mean Base flow (cfs)[a]
Green River – Flaming Geyser	294
Newaukum Creek	19.7
Soos Creek	26.7
Mill Creek	1.2
Black River	~5
Green River – Foster Links	291

[a] Section 2.2 presents specific flow gages or flow measurement methods for each sample location.

Daily precipitation, chemical, and TSS data for both main stem Green River locations and Soos and Newaukum creeks were plotted against daily mean flow over the sampling period (Appendix D, Figures D1-D5). These plots illustrate that over the course of the study period, samples were collected during storms of varying intensities. However, it is important to note that the highest flows in the main stem Green River do not necessarily correspond to the greatest rainfall events due to water releases from the Howard Hanson Dam. For example the highest flow condition (2/24/2012) was not associated with the greatest rainfall event. For the tributaries, these plots demonstrate that comparable rainfall will elicit a greater flow later in the wet season than early in the wet season (October – November).

5.8 Relationships between Parameters

As previously discussed in Section 4.3 correlation analysis was used to explore relationships between select chemical and physical parameters. This section provides a summary of the significant findings of the correlation analysis; a complete presentation of the correlation analysis can be found in Appendix D.

A significant positive correlation between total arsenic and TSS (Spearman: R_s=0.909, $p<0.001$) (Figure 22) was observed for the combined Green River main stem sites. A significant and moderately predictive correlation was also observed between total arsenic and mean flow over the sampling period (Pearson: R_s=0.79, $p<0.05$) at the main stem sites; however, dissolved arsenic was not significantly correlated to TSS or mean flow. This finding is further supported by the plots that compare arsenic concentrations and average daily flow over time for the main stem sites (Figures D-5 and D-7, Appendix D). Particulate arsenic[7] was significantly correlated with TSS during storm events at the main stem sites with the same predictive power as that observed for total arsenic (Spearman: R_s=0.909, $p<0.001$; Appendix D).

[7] Based on the difference between total and dissolved arsenic on per sample basis.

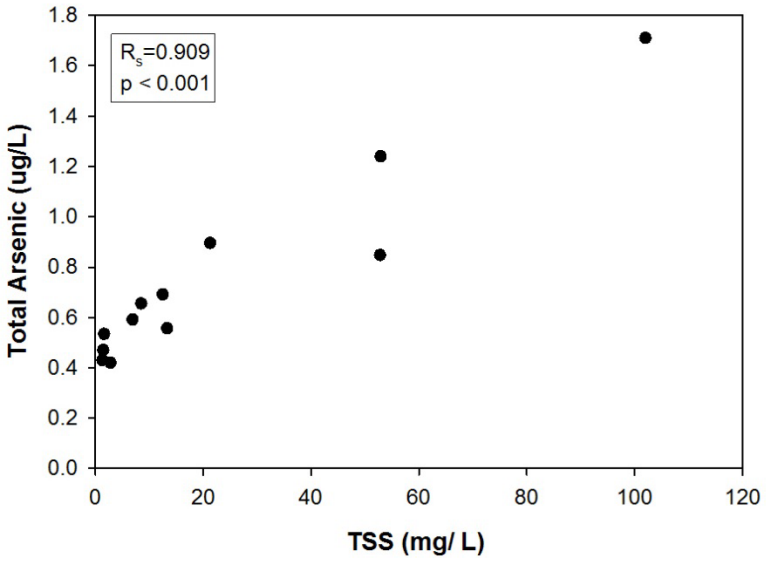


Figure 22. Relationship between Total Arsenic and TSS for the Green River Main stem Sites during Storm Events

For the tributaries, both total and dissolved arsenic were significantly and moderately correlated with TSS during storm events (Spearman: R_s=0.750, p<0.001 and R_s=0.548, p<0.05, respectively). Total arsenic was also significantly correlated to TOC and DOC, but these relationships were only moderately predictive (Spearman: R_s=0.586, p<0.05 and R_s=0.500, p<0.05, respectively). Plots of chemistry, TSS, precipitation and flow for Newaukum, Soos creeks and the main stem sites are included in Appendix D (Figures D-1 to D-10).

PAH compounds were selected for correlation analysis based on frequency of detection across sites. For the Green River main stem and tributaries, some individual PAHs were correlated with physical parameters; however, all PAH correlation results should be interpreted with caution because only detected PAH concentrations were included in analysis. Because of this, the results of the correlation analyses are only presented in Appendix D for the PAH compounds.

Total PCBs in the Green River main stem sites under storm event conditions were not significantly correlated with precipitation, average flow, or conventional parameters (p>0.05). The degree of water releases and associated suspended solids from the Howard Hanson Dam maybe influencing these relationships. For the tributaries, total PCBs were significantly and moderately correlated with TSS, TOC, and DOC during storm events (Spearman: R_s=0.731, p<0.001; R_s=0.740, p<0.0001; and R_s= 0.649, p<0.01, respectively). While PCBs are typically associated with organic carbon and fine particulates due to their hydrophobic nature, the moderate relationship observed here suggests there may be other factors influencing total PCB concentrations. Combining data from the three tributaries may also influence correlation findings, because of the potential for varying PCB sources and pathways in the individual tributary basins. Data presented in Appendix D, plotting PCB concentrations and average daily flow over time for the main stem sites, suggest that flow may not be a driving factor in PCB concentrations for the main stem Green River

locations. Similar plots for Newaukum and Soos creeks are also presented in Appendix D, although these were not significant correlations for the tributaries.

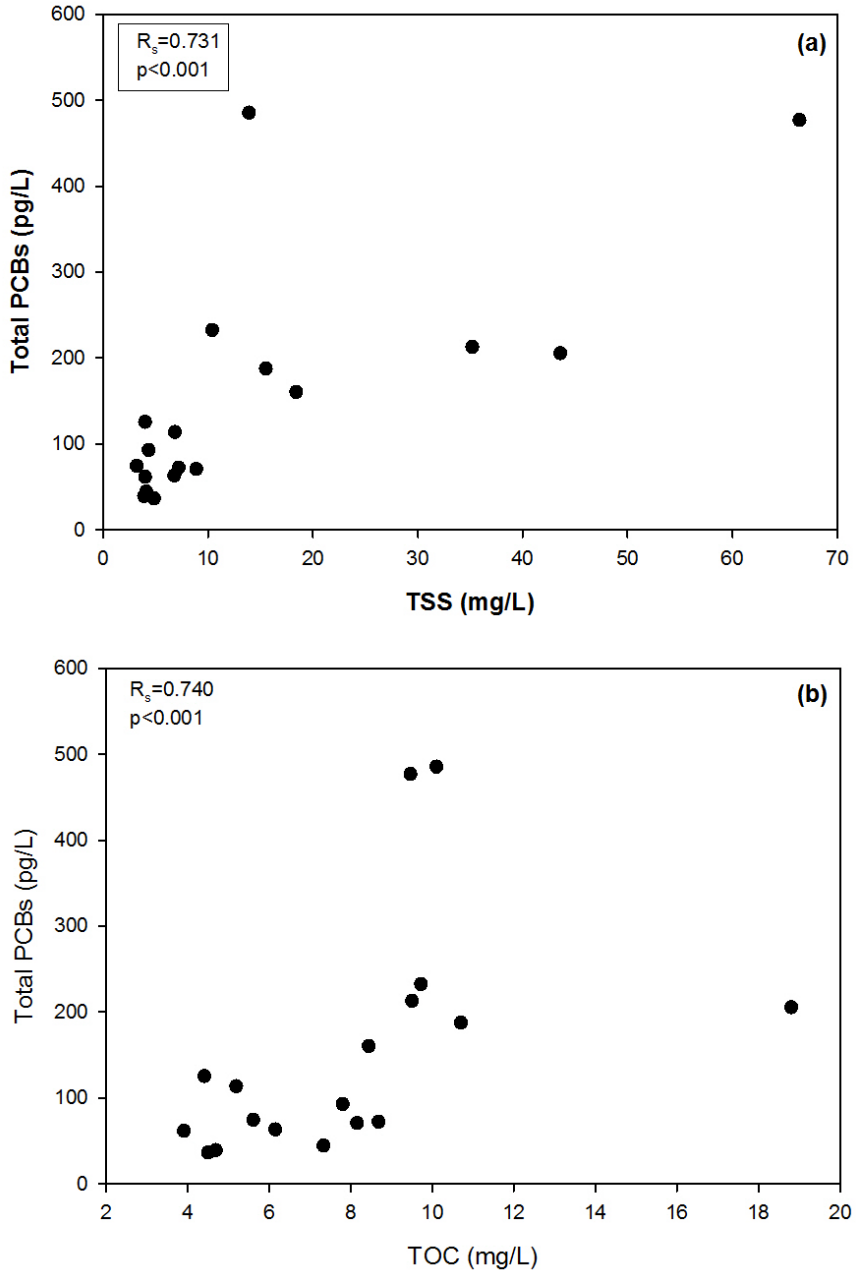


Figure 23. Relationship between Total PCBs and (a) TSS and (b) TOC for Newaukum Creek, Soos Creek, and Mill Creek during Storm Events

TSS concentrations in the two Green River main stem sites were strongly correlated with average flow over the sampling period (Spearman: R_s=0.944, p<0.001) (Figure 24). This was not a significant correlation for the tributaries. Higher flows in the Green River main stem can be caused by storm events and/or significant water releases from the Howard Hanson Dam, both of which can result in elevated suspended solids concentrations. This is

further supported by data presented in Appendix D, which includes plots of TSS and average daily flow over time for the main stem sites.

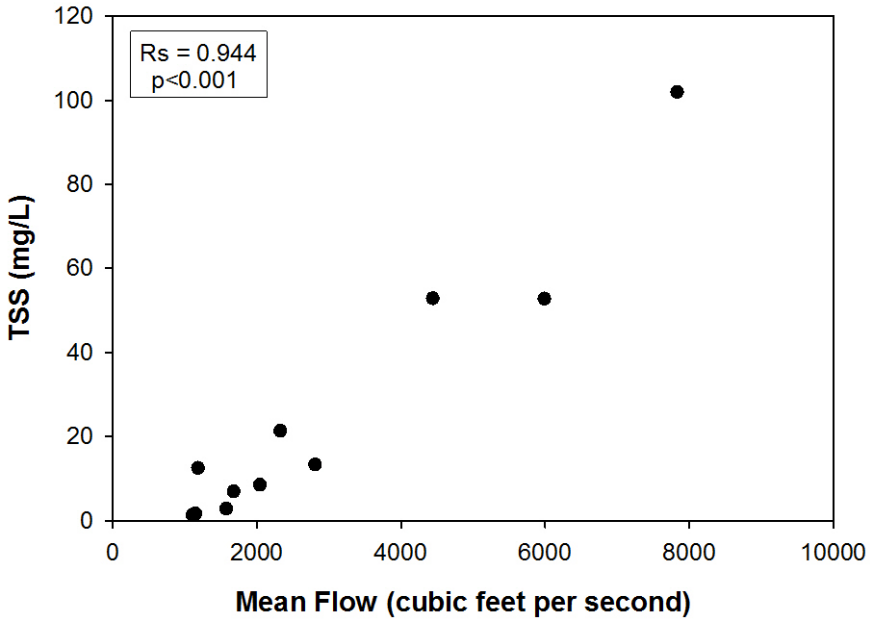


Figure 24. Relationship between TSS and Average Flow over the Sampling Period for the Two Green River Main stem Sites

While TSS concentrations in the two Green River main stem sites were not significantly correlated with precipitation over sampling period, TSS concentrations were significantly and moderately correlated with precipitation for the tributary sites (Spearman: R_s=0.490, $p<0.05$). Precipitation was not significantly correlated with any of the chemistry parameters (see Appendix D). For the Green River main stem sites, the dataset is influenced by two significant Dam releases that affected correlation analysis such that a pattern with precipitation was not observed. If more samples were collected during storm events without significant Dam releases, it is possible a relationship with precipitation might be observed.

6.0. SAMPLING METHOD EVALUATION

This section presents the results of the sampling method evaluation. As previously discussed, the purpose of this comparison was to determine if use of an autosampler effectively characterizes the water quality conditions in the main stem Green River. Data for all parameters presented in tables and figures represent the mean of three samples, with the exception of PCBs, for which only one sample was analyzed for each sampling condition. Due to the small sample size statistical analyses were not conducted on these data.

Total and dissolved arsenic concentrations measured using the two sampling methods were similar during both storm and baseflow conditions. The respective mean RPDs for total and dissolved arsenic were 2.2% and 2.4% under baseflow conditions and 2.6% and 1.1% for storm event samples (Table 19).

PAHs were evaluated as individual compounds rather than total LPAH and total HPAH because of the low detection frequency of most PAH compounds. Based on their relatively high frequency of detection in both sample types, two LPAH (acenaphthylene and anthracene) and two HPAH (chrysene and benzo(b,j,k)-fluoranthene) compounds were selected for analysis. For these PAHs, if the compound was detected in only one sample type, the RPD was calculated using the MDL to represent the non-detect PAH compound (Table 19).

For many individual LPAHs and HPAHs, both samples types had no detections. Mean RPDs for the two selected LPAH compounds ranged from 13% (anthracene) to 17% (acenaphthylene) during storm events. During baseflow conditions, acenaphthylene had a mean RPD of 8.2%; an RPD for anthracene was not calculated because it was only detected in one of three samples collected with an autosampler and not detected in the three cross-section composite samples. Mean RPDs for the two selected HPAH compounds ranged from 11% (chrysene) to 13% (benzo[b,j,k]fluoranthene) for storm events. During baseflow conditions, chrysene had a mean RPD of 46%; an RPD for benzo(b,j,k)fluoranthene was not calculated because it was only detected in three samples (two collected by autosamplers and one cross-section composite). Most of these RPDs are within the SAP quality control acceptance criteria of 40% for laboratory duplicate samples.

Table 19. Data Summary for Samples Collected by Autosampler vs. Cross-section Composite by Flow Condition

Parameter[b]		FOD	Flow	Mean Concentration[a]		Mean RPD
				Autosampler	Cross-section Composite	
Dissolved As (µg/L)		3/3	Base	0.658	**0.662**	2.2%
		3/3	Storm	**0.588**	0.584	2.6%
Total As (µg/L)		3/3	Base	0.767	**0.782**	2.4%
		3/3	Storm	**0.799**	0.794	1.1%
LPAHs	Acenaphthylene (µg/L)	3/3	Base	**0.00053 J**	0.00048 J	8.2%
		3/3	Storm	**0.00081 J**	0.00071 J	17%
	Anthracene (µg/L)	3/3	Storm	**0.00097 J**	0.00085 J	13%
HPAHs	Benzo(b,j,k)-fluoranthene (µg/L)	3/3	Storm	**0.0086 J**	0.0079 J	13%
	Chrysene (µg/L)	1/3,2/3[c]	Base	0.00025 J	**0.00038 J**	46%
		3/3	Storm	0.0033 J	0.0033 J	11%
DOC (mg/L)		3/3	Base	1.88	**1.97**	5.4%
		3/3	Storm	**3.69**	3.63	2.2%
TOC (mg/L)		3/3	Base	**2.44**	2.32	10%
		3/3	Storm	**4.63**	4.07	13%
TSS (mg/L)		3/3	Base	3.05	**3.60**	23%
		3/3	Storm	7.43	**7.77**	7.8%

RPD – Relative percent difference, FOD – Frequency of Detection

J - Value estimated; **Bolded values signify the higher mean between method types.**

[a] For arsenic and conventionals, concentrations are based on a mean of three samples. For PAH compounds, MDLs were used for non-detect concentrations for calculations. RPDs were not calculated if concentrations detected for both methods were below MDL. For total PCBs, only one sample was collected per flow condition and sample type.

[b]For LPAHs and HPAHs, only two compounds were included in this table. These were chosen based on relatively high FODs.

[C] FOD is 1/3 for autosampler and 2/3 for cross-section composite.

Total PCB results differed greatly between sampling methods during baseflow, with an RPD of 177% (Table 20). The autosampler method yielded the higher PCB concentration in both the baseflow and storm event sample pairs. The three most influential congener groups were PCB-44/47/65, PCB-45/51, and PCB-68 in both autosampler samples. These congeners were much less influential in the cross-sectional hand composite samples (Table

20). Subsequent studies have shown that congeners within these coeluting groups (i.e., PCB-47, PCB-51, and PCB-68) are indicative of contamination from silicone tubing.

While these sample pairs were intended to compare results from composite samples collected at one point versus as a cross-section to the river, another difference is the degree of exposure to silicone tubing. The autosampler composite samples were exposed to silicone tubing throughout sampling, while the cross-sectional composites were exposed to silicone tubing only during the sample splitting process (Section 2.3.3 and Section 2.4). Even after adjusting for the equipment contamination, baseflow results differed substantially between sampling methods, which could be due to environmental variability (Table 20). However, the storm event samples were similar and the RPD was within acceptable analytical variability.

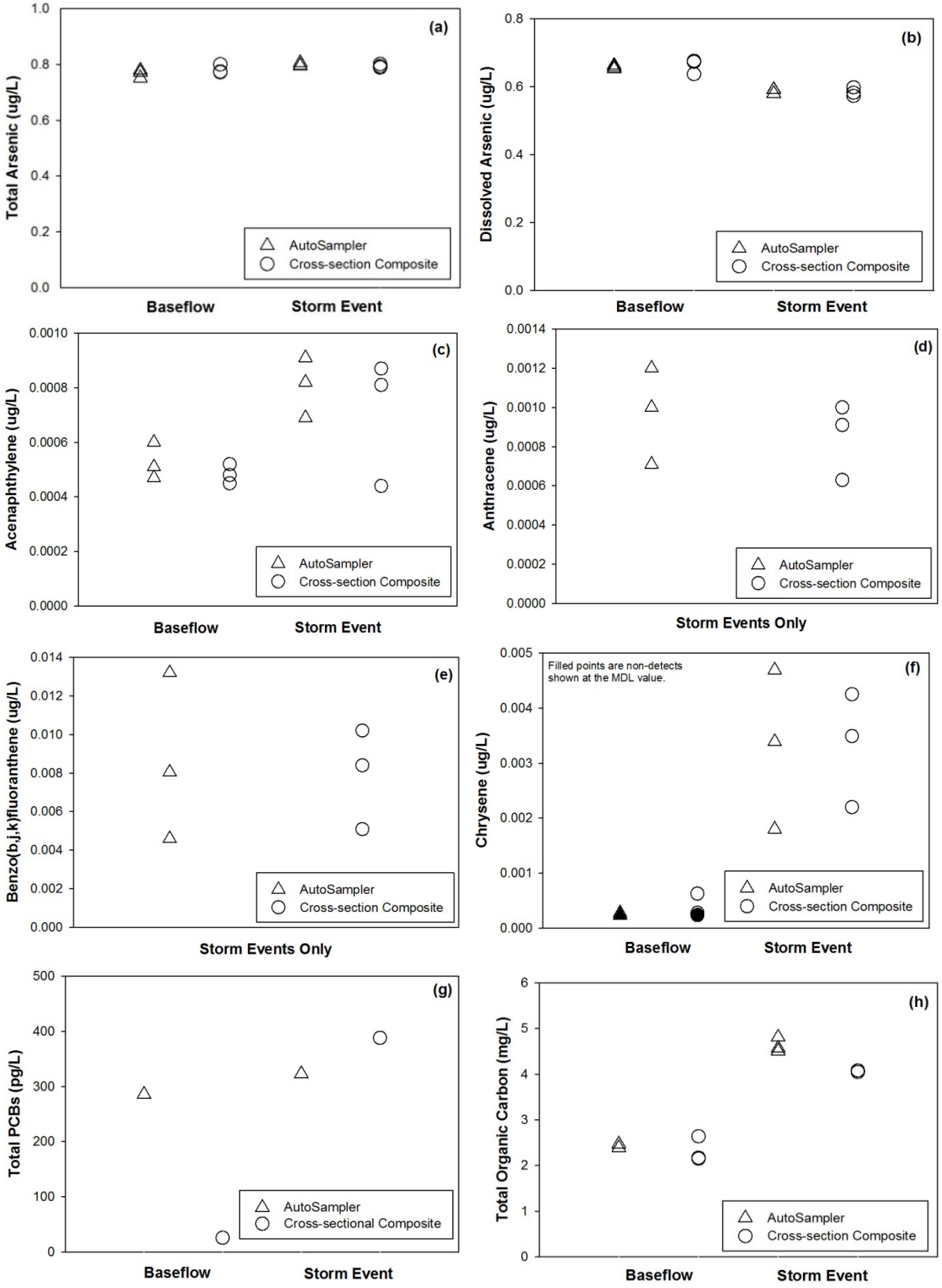
Table 20. PCBs Results in Samples Collected by Autosampler vs. Cross-section Composite by Flow Condition

Parameter	FOD	Flow	Concentration (pg/L)		RPD
			Autosampler	Cross-section Composite	
Total PCBs	1/1	Base	754 J	45.3 J	177%
	1/1	Storm	542 J	423 J	25%
Sum of PCB-44/47/65, PCB-45/51, PCB-68	1/1	Base	469 J	19.4 J	184%
	1/1	Storm	219	35.3 J	145%
Adjusted Total PCBs [a]	1/1	Base	286 J	25.9 J	167%
	1/1	Storm	323 J	388 J	18%

[a] PCB totals without PCB-44/47/65, PCB-45/51, PCB-68.

DOC, TOC and TSS concentrations were very similar in samples collected using both sampling methods. During baseflow conditions, mean RPDs for DOC, TOC, and TSS were 5.4%, 10.1% and 23.0% respectively. RPDs for samples collected during storm events for DOC, TOC and TSS were 2.2%, 12.8% and 7.8% respectively. All of these RPDs fall within the SAP quality control acceptance criteria for laboratory duplicate samples

In general, this analysis indicates that use of autosamplers is an adequate sampling method to characterize conditions in the Green River - Foster Links location. However, there is some uncertainty for PCBs under baseflow conditions where greater differences were observed between the two collection methods (based on adjustments for PCB equipment contamination). However, because only one baseflow and one storm event sample are available for this analysis, definitive conclusions cannot be drawn regarding sample method biases. Results of the two sampling methods are illustrated in Figure 25.


(a)
Total Arsenic (ug/L)
1.0
0.8
0.6
0.4
0.2
0.0
AutoSampler
Cross-section Composite
Baseflow
Storm Event
(b)
Dissolved Arsenic (ug/L)
0.8
0.6
0.4
0.2
0.0
AutoSampler
Cross-section Composite
Baseflow
Storm Event
(c)
Acenaphthylene (ug/L)
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
AutoSampler
Cross-section Composite
Baseflow
Storm Event
(d)
Anthracene (ug/L)
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
AutoSampler
Cross-section Composite
Storm Events Only
(e)
Benzo(b,j,k)fluoranthene (ug/L)
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
AutoSampler
Cross-section Composite
Storm Events Only
Filled points are non-detects shown at the MDL value.
(f)
Chrysene (ug/L)
0.005
0.004
0.003
0.002
0.001
0.000
AutoSampler
Cross-section Composite
Baseflow
Storm Event
(g)
Total PCBs (pg/L)
500
400
300
200
100
0
AutoSampler
Cross-sectional Composite
Baseflow
Storm Event
(h)
Total Organic Carbon (mg/L)
6
5
4
3
2
1
0
AutoSampler
Cross-section Composite
Baseflow
Storm Event

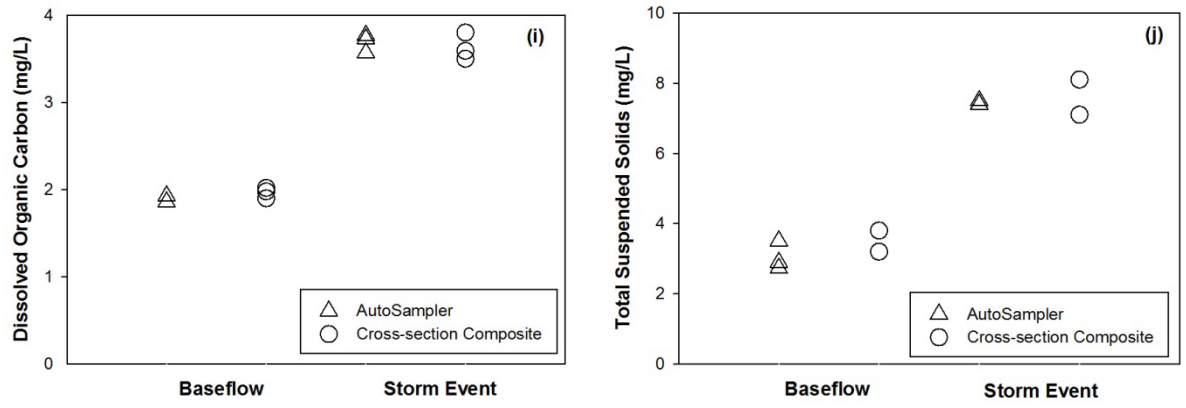


Figure 25. Autosampler and Cross-sectional Composites during Baseflow and Storm Events: Concentrations of Total Arsenic (a), Dissolved Arsenic (b), Naphthalene (c), Chrysene (d), PCBs (e), TOC (f), DOC (g) and TSS (h)

7.0. DISCUSSION AND CONCLUSION

This section presents a comparison of baseflow and storm event water quality conditions within the Green River Watershed as well as a comparison of general differences observed between sampling sites. Also included here is a discussion outlining the comparison of data from this study to data from another regional study. Finally, overall findings are summarized followed by summaries of current sampling efforts and recommendations for further work.

The primary goals of this effort were to compare concentrations of arsenic, PAHs and PCBs between dry season (baseflow conditions) and wet season (storm events) and evaluate relative differences in chemical concentrations in the Green River and its major tributaries. Sections 7.1 and 7.2 provide a discussion related to these goals. In addition to comparing and contrasting data from this study, data are also compared to findings of the Green-Duwamish WQA (Herrera 2005). As previously mentioned the Green-Duwamish WQA was conducted in 2003 to evaluate water quality conditions in the Green River Watershed and included collection and analysis of storm event and baseflow samples from both the main stem Green River and associated tributaries. However, due to analytical detection limitations, only data for arsenic and conventional parameters are comparable to data collected by this study. Section 7.3 presents a comparison of Green River data from this study compared to previous Green River water chemistry results from the LDW RI. Section 7.4 provides a comparison of data from this study to data collected from two other large river systems in the Puget Sound Basin, and other general findings of this study are discussed in Section 7.5. Finally, Section 7.6 presents the key findings, summaries of current sampling efforts and recommendations for future work.

7.1 Comparison of Baseflow and Storm Event Conditions

The two main stem Green River locations are influenced by dam releases and represent much larger drainage areas relative to the tributaries evaluated here. As a result, the hydrodynamics and source inputs associated with these systems are expected to be different. Based on these differing conditions, comparison of baseflow to storm event conditions were evaluated separately for main stem Green River sites and the tributaries. The Black River was also evaluated separately from the other tributaries because the Pump Station creates unique hydrological conditions (see Section 2.1).

To demonstrate the magnitude of differences between storm event and baseflow concentrations, ratios of mean storm event to baseflow concentration for each parameter were calculated and graphed. In addition, as discussed in Section 4.1.3, statistical differences were evaluated for baseflow versus storm event conditions.

Of the parameters evaluated, the greatest differences between mean storm event and baseflow concentrations were observed for TSS where mean storm event concentrations were higher for all location groups (i.e., main stem, tributaries, and Black River) (Figures 26, 27, 28). This difference was statistically significant for the combined

tributaries ($p<0.001$) and the Black River ($p<0.05$). The relative difference between storm event and baseflow concentrations was small for the Black River, which was likely influenced by collection of storm event samples from the pooled area behind the dam. There were no statistical differences between baseflow and storm event TSS concentrations at the main stem sites, which could be influenced by the high variability of the storm event concentrations. The Green-Duwamish WQA also compared baseflow to storm event conditions; however, statistical differences were not tested for these comparisons. The Study found higher median TSS concentrations during storm events when compared to baseflow conditions (Herrera 2005). In addition, while DOC concentrations were not very different under baseflow and storm conditions, the Green-Duwamish WQA study found TOC concentrations were consistently higher during storm events.

Mean total arsenic concentrations were slightly higher under baseflow conditions than during storm events for all location groups except the Black River, where they were very similar. These slight differences were not statistically significant ($p>0.05$), although the t-test for Black River data had power less than 0.80, indicating there was a lower probability of identifying a statistical difference if one existed.

With the exception of the Black River, mean dissolved arsenic concentrations were greater during baseflow conditions than storm events (Figures 26, 27, 28). This difference was statistically significant for the combined main stem and the three combined tributaries ($p<0.001$ and $p<0.01$, respectively). The lower dissolved arsenic concentrations observed during storm events may be due to dilution of the naturally occurring arsenic present in these water bodies. The mean dissolved arsenic concentrations in Black River storm event samples were statistically higher than levels in baseflow samples ($p<0.05$). With the possible exception of the Black River, baseflow arsenic concentrations were dominated by the dissolved fraction; this pattern was not consistently observed in storm event samples where the dissolved fraction was more variable between sites and events. For both total and dissolved arsenic, differences in storm and baseflow mean concentrations were small and could be a function of analytical or environmental variability. The Green-Duwamish WQA did not test statistical differences in total or dissolved arsenic concentrations between storm and baseflow conditions (Herrera 2005).

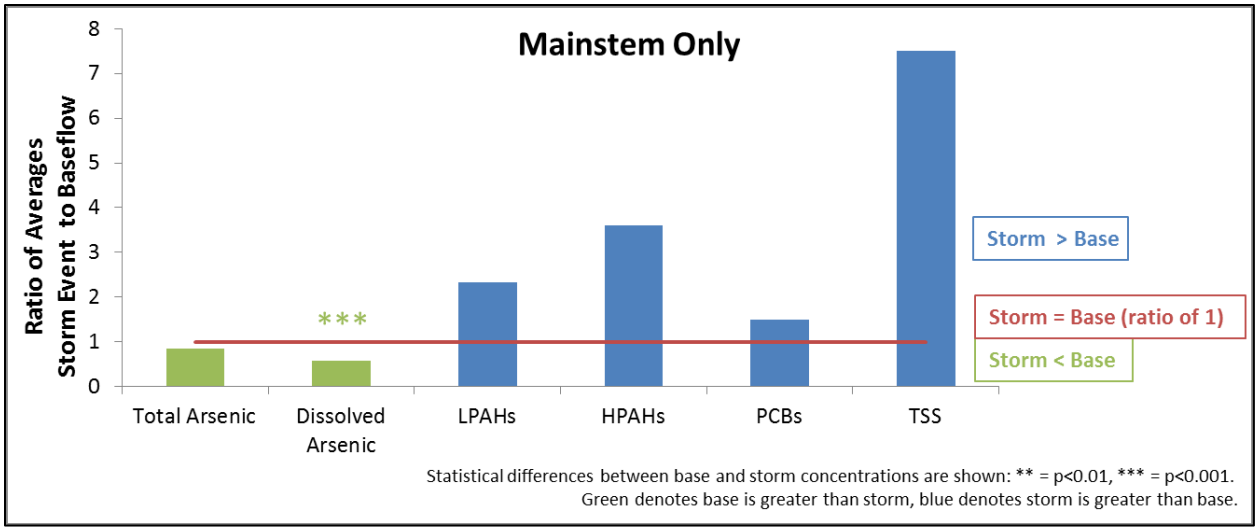


Figure 26. Mean Storm Event Concentrations Relative to Mean Baseflow Concentrations for the Two Green River Main stem Sites Combined

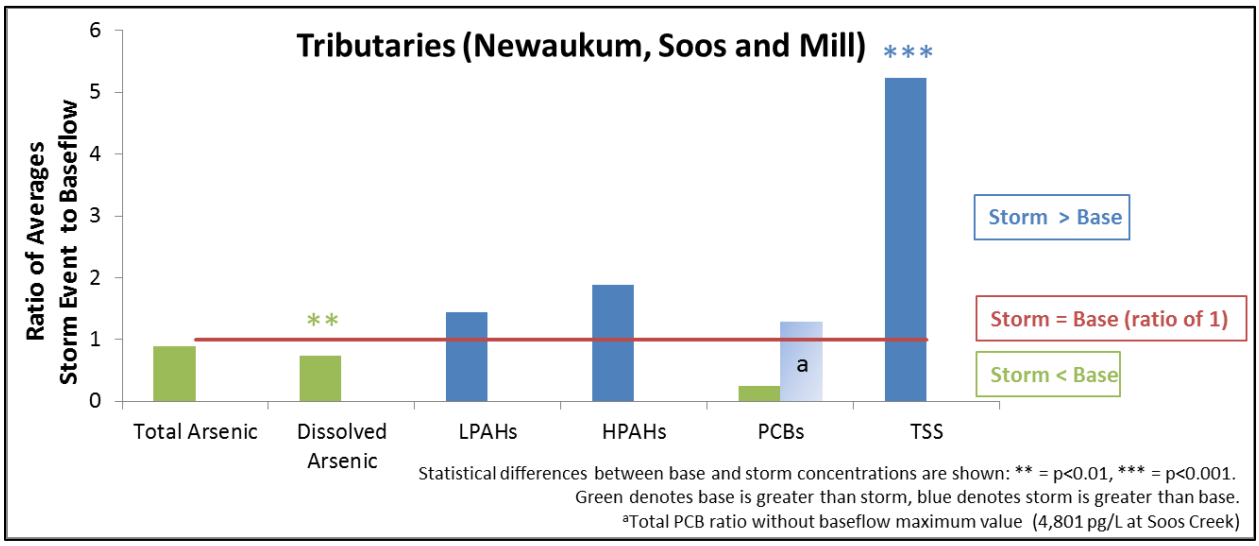


Figure 27. Mean Storm Event Concentrations Relative to Mean Baseflow Concentrations for the Newaukum, Soos and Mill creeks Sites Combined

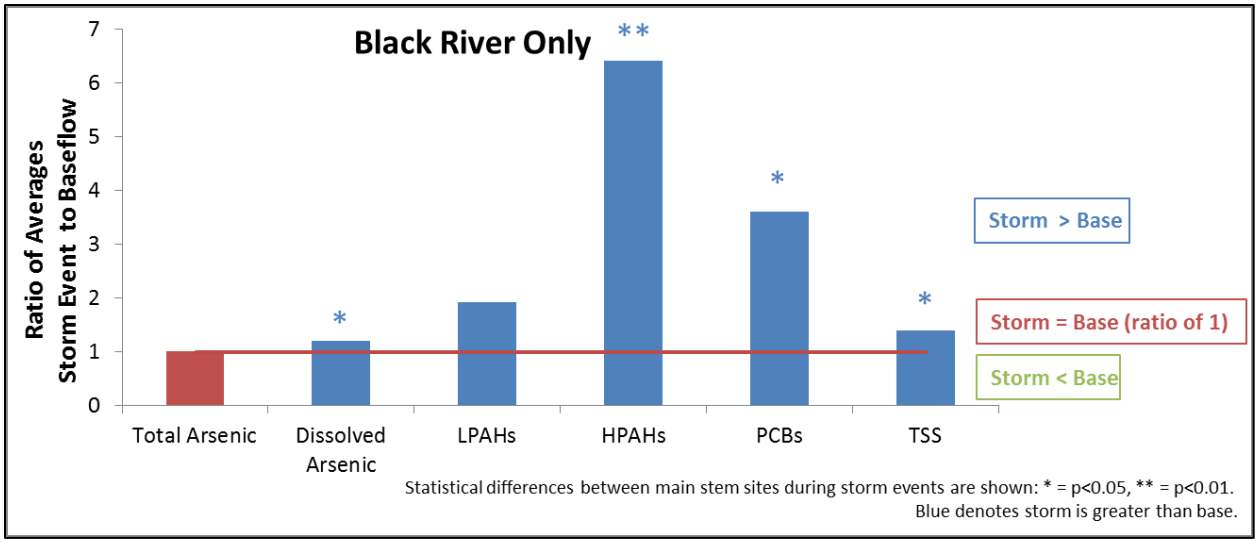


Figure 28. Mean Storm Event Concentrations Relative to Mean Baseflow Concentrations for the Black River Site Only

For all location groups, mean LPAH and HPAH concentrations during storm events were greater than levels measured during baseflow conditions (Figures 26, 27, 28). These differences were not statistically significant, except for HPAH concentrations in the Black River ($p<0.01$) (Figure 28). The t-tests for LPAHs for both the mainstem and Black River had statistical power less than 0.80, indicating there was a lower probability of identifying a statistical difference if one existed. It is important to keep in mind that the frequency of detection and detected concentrations in these samples were very low. Additional data collection and analysis would be necessary to better understand the potential for storm event conditions to influence PAH concentrations.

In Black River storm event samples, mean total PCB concentrations were statistically greater than those detected in baseflow samples (Figure 28; $p<0.05$). For the combined main stem sites, mean total PCB concentrations were slightly higher during storm events but there were no statistically significant differences. For the combined tributaries, mean total PCB concentrations were slightly higher under baseflow conditions; however, this finding was highly influenced by one baseflow sampling event in Soos Creek where total PCB concentrations were approximately 100 times higher than levels detected in the next highest baseflow sample at this site. When this data point is excluded, the total PCB storm event concentrations in the tributaries were generally higher than levels detected under baseflow conditions, but there were no statistically significant differences (Figure 27).

7.2 Relative Concentration Differences between Locations

The magnitude of difference in mean concentrations between locations during baseflow conditions is presented in Figure 29; mean differences during storm event conditions are illustrated in Figures 30-32. These figures present the ratio of each site mean concentration

to the lowest site mean concentration for each parameter (by sample type). In addition, as discussed in Section 4.1.3, statistical differences between sites were evaluated for storm event conditions; due to small sample sizes, statistical analysis was not conducted to compare baseflow concentrations.

The highest mean DOC and TOC levels were observed in Mill and Newaukum creeks during storm events; concentrations were up to approximately four times as high as levels in the other locations (Figure 30). The lowest levels of DOC and TOC during storm events were detected at the Green River – Flaming Geyser location. For both DOC and TOC, storm event concentrations were statistically higher in Mill Creek than at both main stem locations. DOC and TOC concentrations were also statistically higher at Newaukum Creek when compared to the Green River – Flaming Geyser location. Some of the highest mean TSS levels were detected in storm event samples from the Green River – Foster Links location, followed by Mill Creek; mean concentrations were about five times those found at the other locations (Figure 30). However, there were no statistical differences in TSS concentration between sites. Under baseflow conditions, mean TSS concentrations were higher at all three downstream locations relative to the three upstream locations (Figure 29). The Green-Duwamish WQA also observed spatial differences in TOC and DOC concentrations between sites and also found no statistical spatial differences in TSS concentrations between stream locations (Herrera 2005).

Of the parameters analyzed, total and dissolved arsenic concentrations were the least variable across locations. Mean baseflow concentrations of total and dissolved arsenic were all within a factor of 2 of each other (Figure 29). During storm events, mean total arsenic concentrations tended to be highest at the three most downstream locations (Mill Creek, Black River and Green River – Foster Links), and were almost twice as high as concentrations detected in the two most upstream sites (Figure 31). Total arsenic concentrations during storm events at Mill Creek were statistically greater than concentrations at the Green River – Flaming Geyser location and Newaukum Creek. Concentrations in the Black River were also statistically greater than Newaukum Creek during storm events ($p<0.05$). During storm events, Mill Creek had the highest mean dissolved arsenic concentration followed by the Black River. These were both statistically greater than storm event concentrations at both Green River main stem sites. Dissolved arsenic concentrations at Mill Creek were also statistically greater than concentrations at Newaukum Creek ($p<0.05$). The Green-Duwamish WQA also found some spatial significant differences in arsenic concentrations between sites (Herrera 2005).[8]

The highest mean LPAH concentration across all sites and sample types was detected in baseflow samples from Soos Creek and was up to six times higher than mean concentrations at the other locations (Figure 29). However, the mean value was highly influenced by one sample with an LPAH concentration (0.101 µg/L) that was higher than levels detected during all other baseflow and storm events. The Green River – Foster Links location and the Black River had the next highest mean baseflow concentrations compared

[8] Similar evaluations were not made for total PCBs or PAHs in the Green-Duwamish Watershed WQA because PCBs were not detected (based on Aroclor analysis) and PAHs were infrequently detected (method sensitivities between studies were not comparable for either of these analytes).

to other sites. LPAH concentrations in storm event samples were less variable between sites than in baseflow samples and no statistical differences between sites were observed (Figure 32).

Detected concentrations of HPAHs were relatively low. The highest mean concentrations were observed during storm events at the three most downstream locations with the Black River being the highest; the mean concentration at this site was up to 54 times as high as levels in the three most upstream locations (Figure 32). During storm events median HPAH concentrations at the Black River and the three most upstream locations were statistically different ($p<0.05$). Mean HPAH concentrations in Black River baseflow samples were highest relative to mean concentrations at the other sampling sites (mean ratio = 7.7) (Figure 29).

Similar to the pattern observed for LPAHs, the highest mean total PCB concentration was also observed in Soos Creek during baseflow conditions; this value was up to 20 times higher than mean concentrations detected at the other locations (Figure 29). Similar to LPAHs, the mean total PCB concentration in Soos Creek during baseflow conditions was highly influenced by one sample with a total PCB concentration that was higher than levels detected in all other baseflow and storm event samples. The next highest PCB concentration was detected in the Black River, which also had the highest mean concentration relative to other sites during storm event conditions. Total PCB storm event concentrations were statistically different in the Black River compared to the Green River – Flaming Geyser site, Newaukum Creek, and Soos Creek (Figure 32).

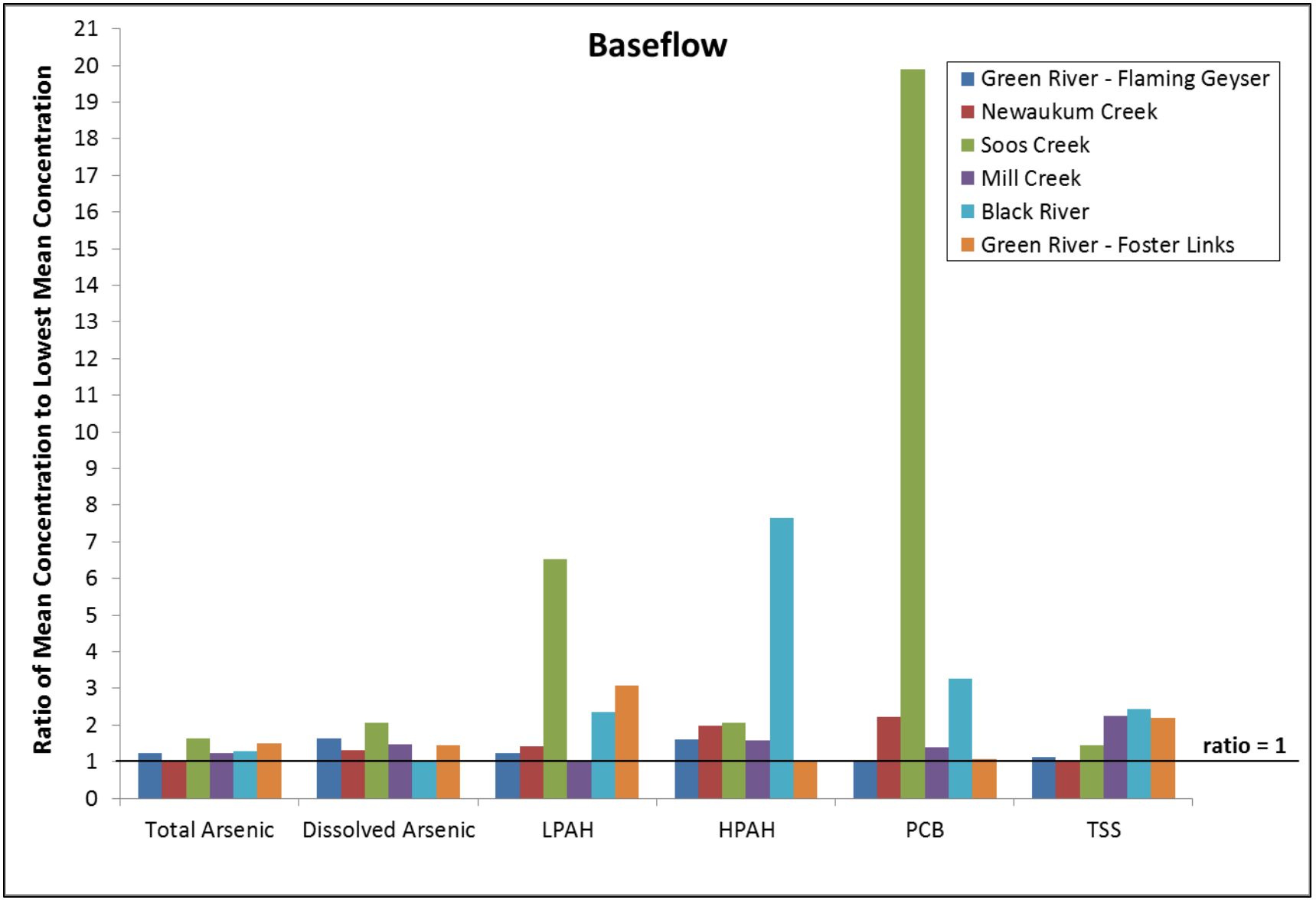


Figure 29. Ratios of Mean Concentrations at Each Site Relative to the Lowest Mean Concentration during Baseflow

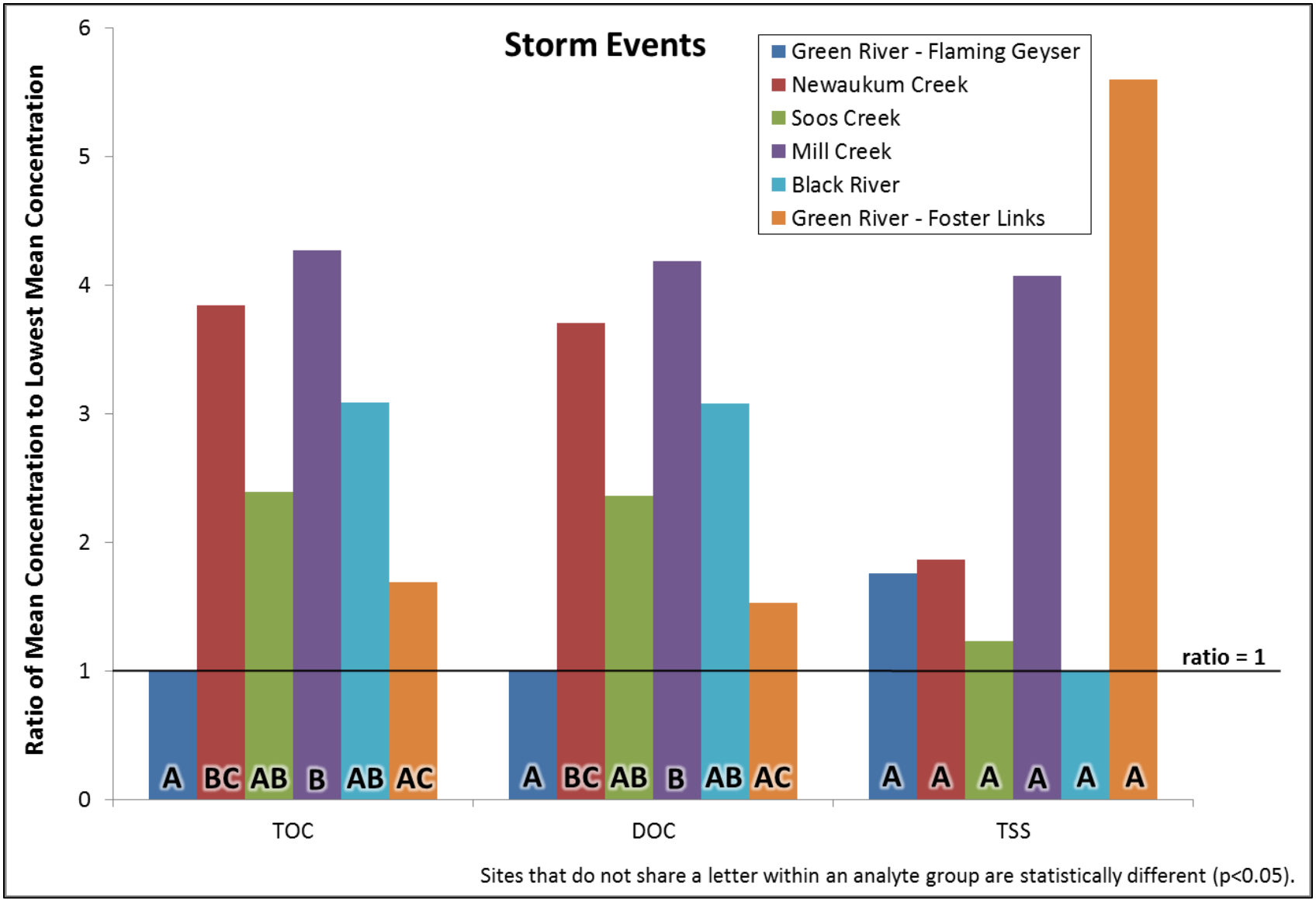


Figure 30. Ratios of Mean Concentrations at Each Site Relative to the Lowest Mean Concentration for Conventionals during Storm Events.

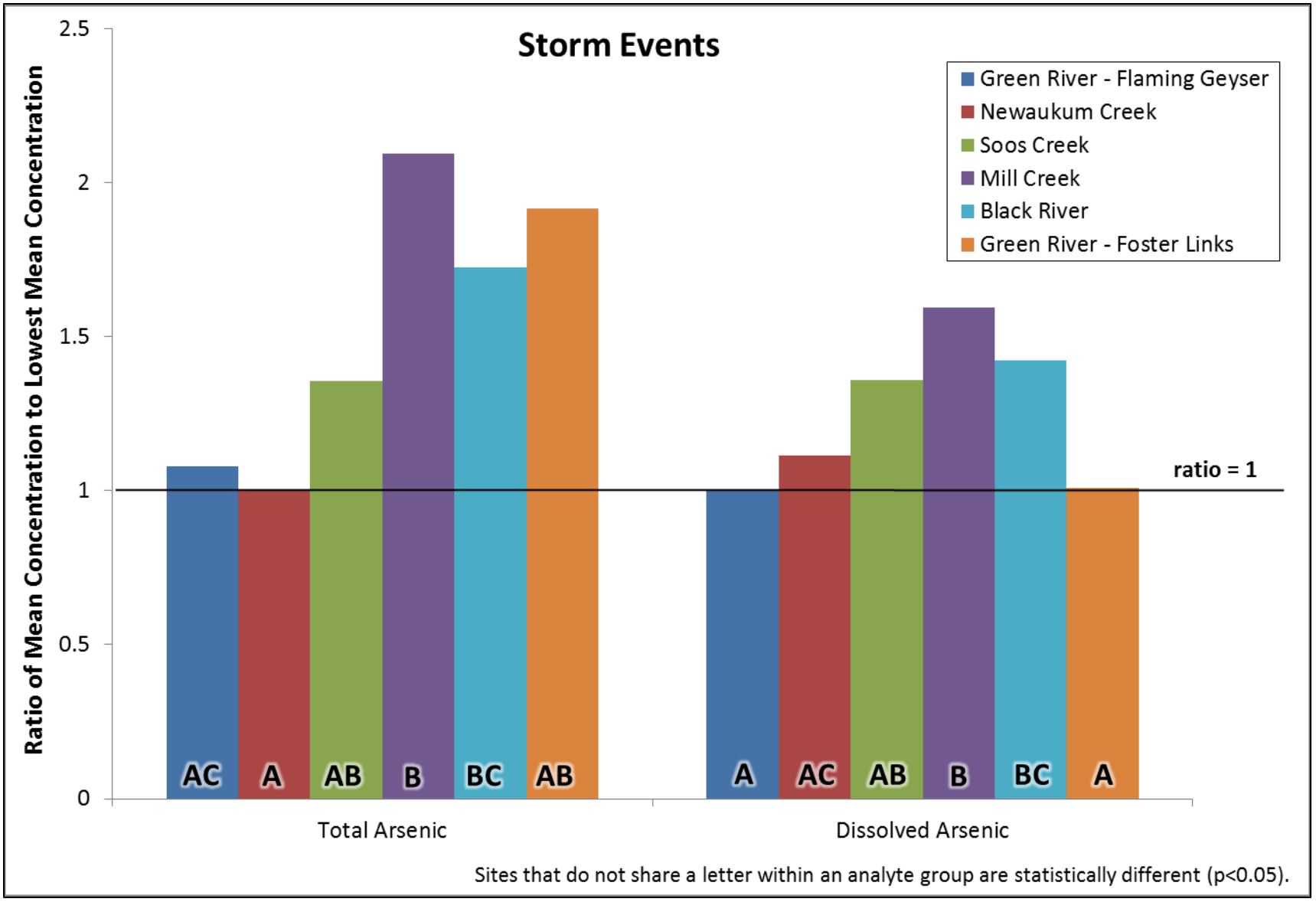


Figure 31. Ratios of Mean Concentrations at Each Site Relative to the Lowest Mean Concentration for Arsenic during Storm Events

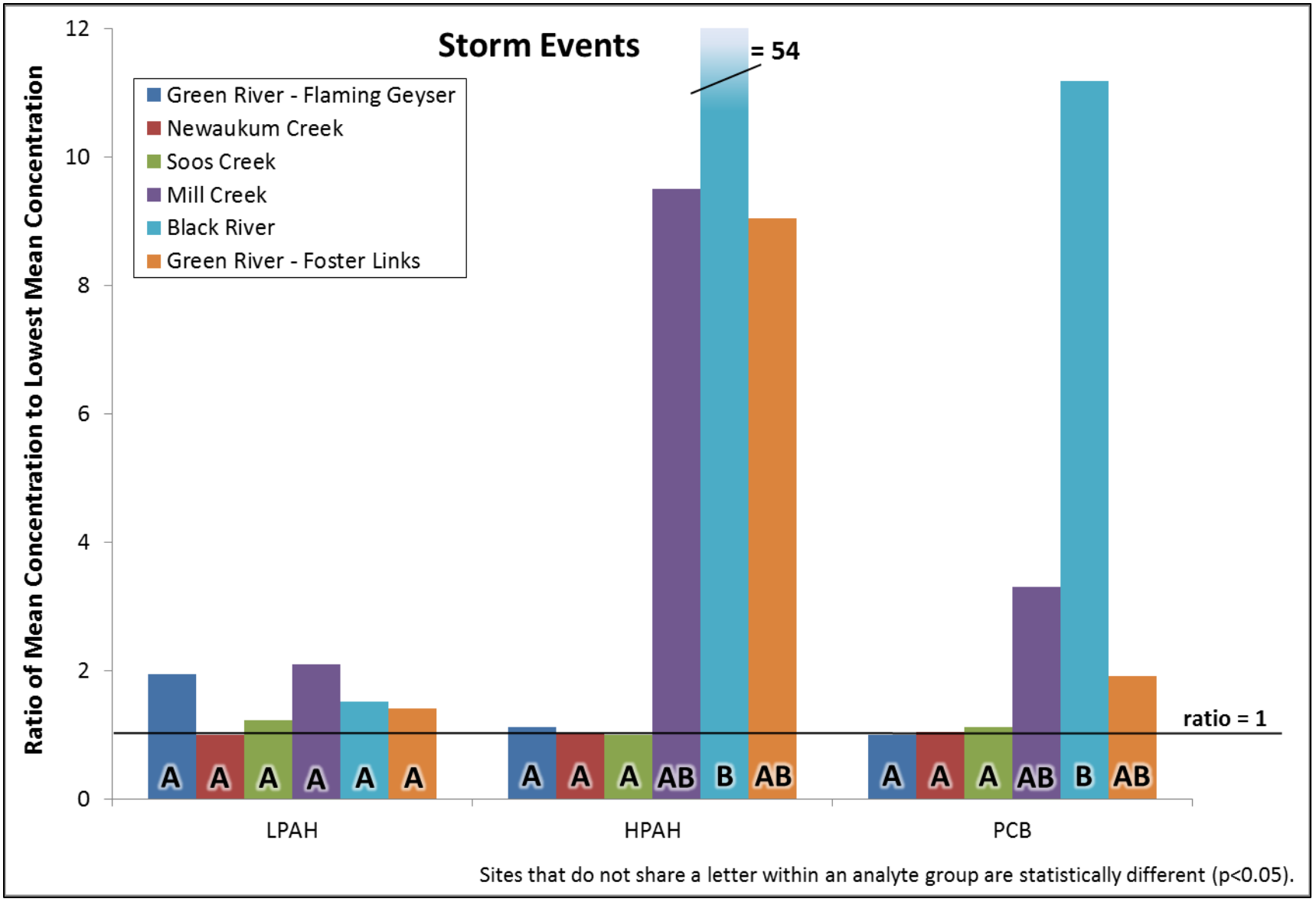
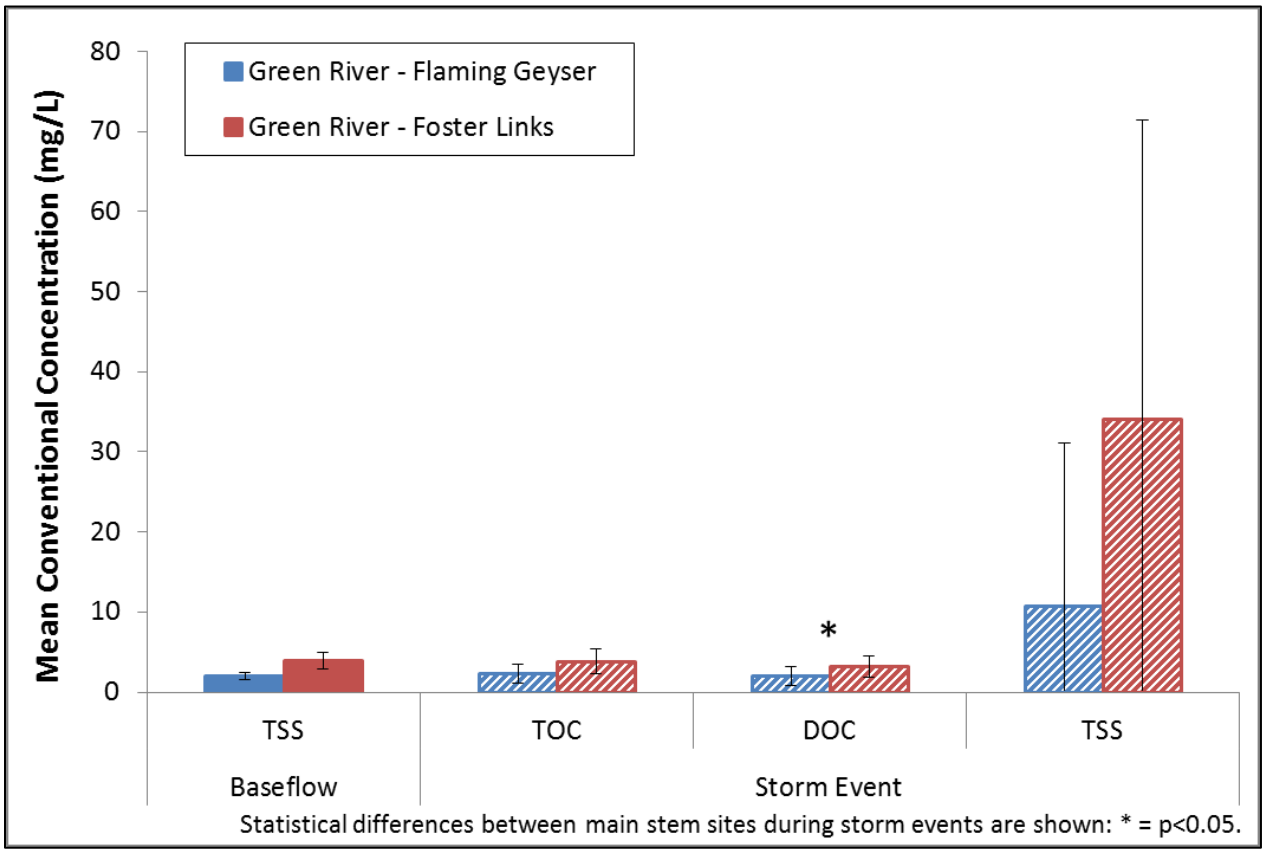


Figure 32. Ratios of Mean Concentrations at Each Site Relative to the Lowest Mean Concentration for Organics during Storm Events

Comparison of storm event data between the upstream and downstream main stem Green River locations indicated that storm event concentrations of DOC, total arsenic and total HPAHs were statistically higher in the downstream location (Foster Links) (Figures 33-36). While most mean storm event concentrations for other parameters were also higher at the downstream location, these differences were not significant.[9] Statistical power was sometimes low due to limited sample size and variable concentrations. For example, while higher mean TSS concentrations were detected at the downstream location, the overlap in the concentration data at the two locations (see error bars in Figure 33), resulted in no significant differences between locations. The most notable exception to this pattern was for total LPAH concentrations, for which the mean concentration during storm events was higher at the upstream site; however, due to high variability, this difference was not statistically significant.

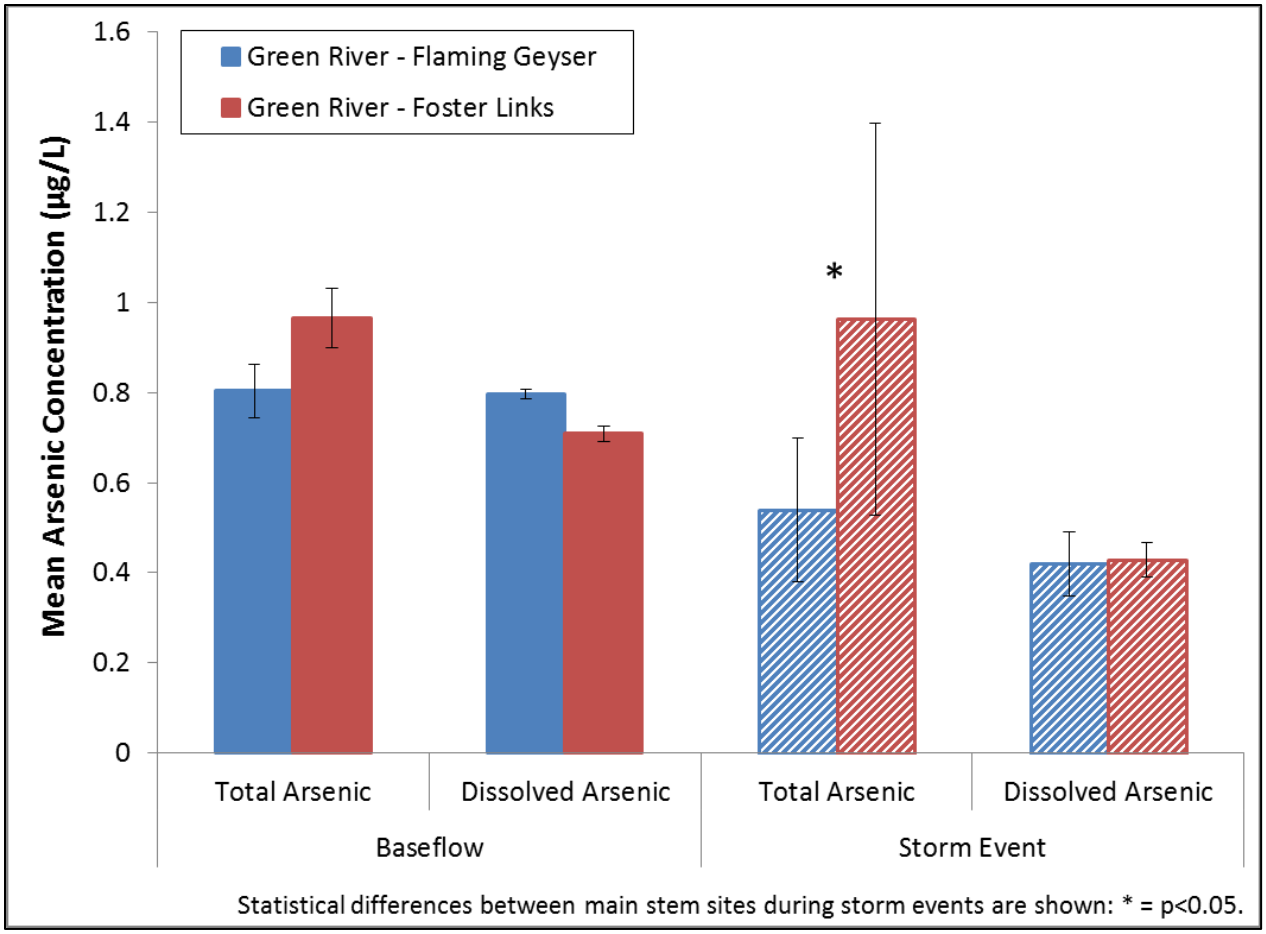
Similar evaluations were performed in the Green-Duwamish Watershed Water Quality Assessment (Herrera 2005): there were no statistical differences observed between upstream and downstream concentrations of dissolved arsenic, DOC or TOC. However, levels of total arsenic were statistically higher at the downstream location during storm events. In addition, TSS concentrations were statistically higher in downstream samples during baseflow conditions; however, no significant differences were observed between the two locations during storm event conditions (Herrera 2005).

[9] Due to small sample size of baseflow events, statistical analyses were not performed.



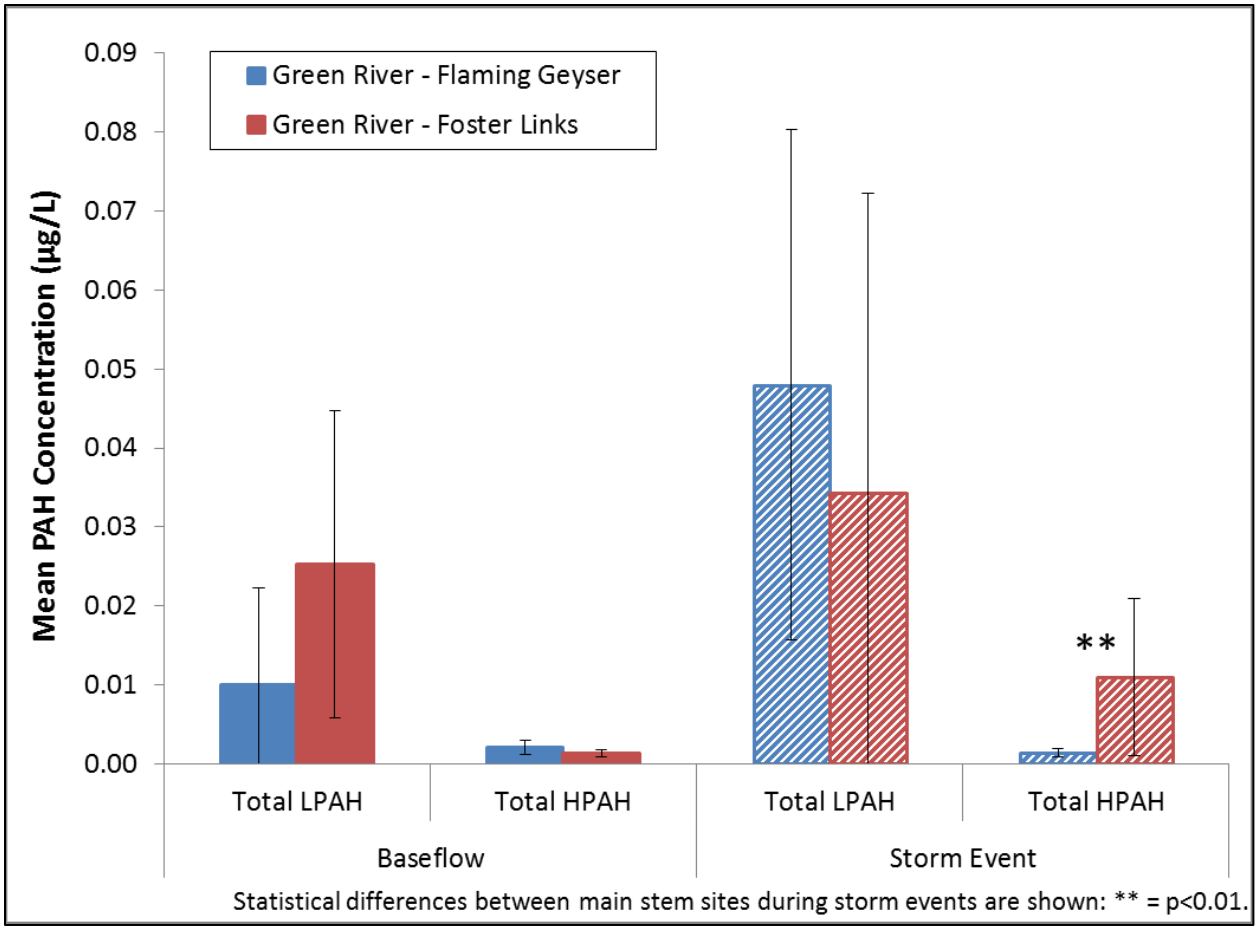
Error bars are standard deviations.

Figure 33. Comparison of Mean TOC, DOC and TSS Concentrations between Upstream and Downstream Green River Sampling Locations



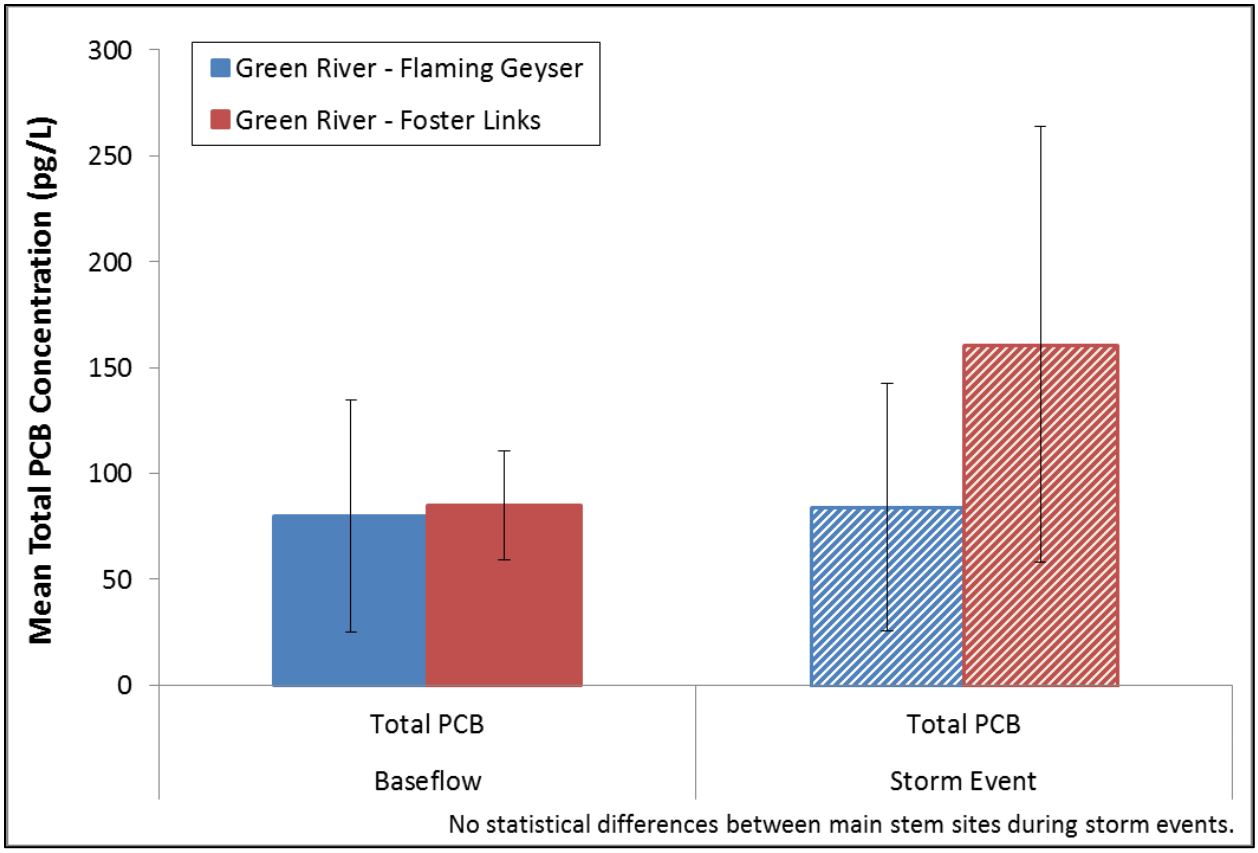
Error bars are standard deviations.

Figure 34. Comparison of Mean Arsenic Concentrations between Upstream and Downstream Green River Sampling Locations



Error bars are standard deviations.

Figure 35. Comparison of Mean Total LPAH and HPAH Concentrations between Upstream and Downstream Green River Sampling Locations



Error bars are standard deviations.

Figure 36. Comparison of Mean Total PCB Concentrations between Upstream and Downstream Green River Sampling Locations

7.3 Comparison to Previous Downstream Green River Sampling Efforts

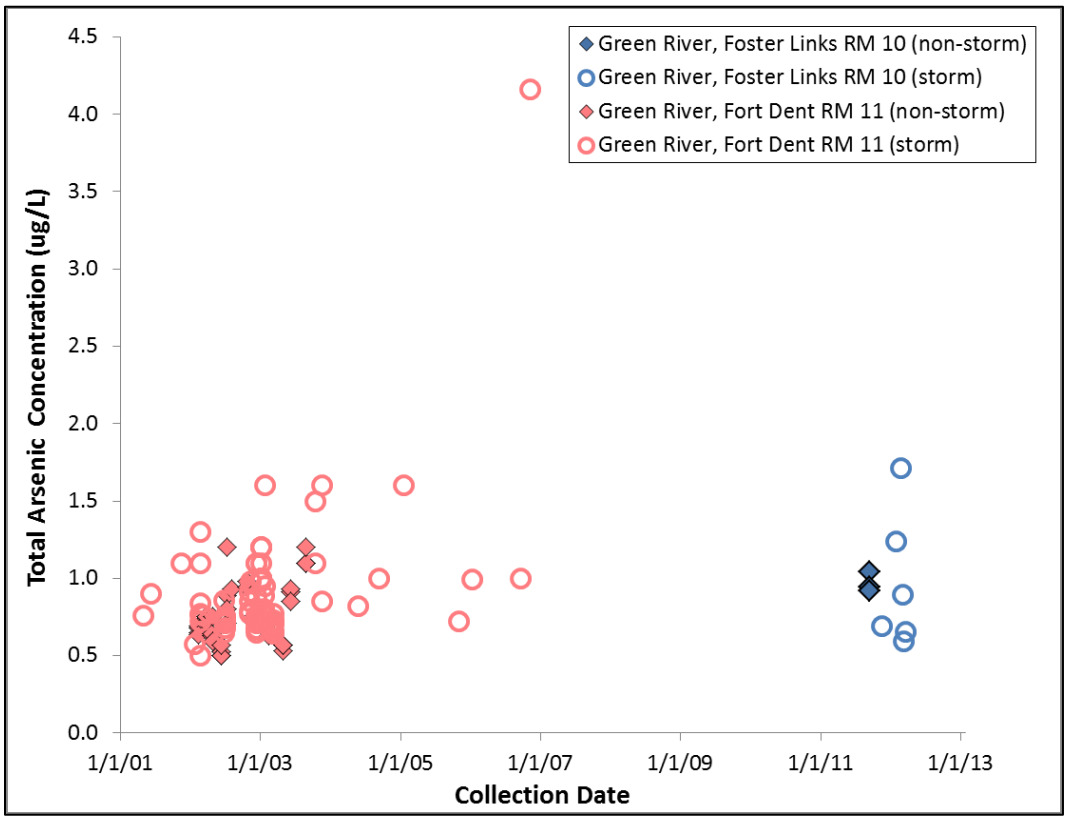
The LDW RI (Windward 2010) summarizes surface water concentrations for total and dissolved arsenic, PAHs and total PCBs (based on congener analysis) in the Green River from previous sampling efforts. The LDW RI includes data for samples collected from the Duwamish River at East Marginal Way Bridge (approximately river mile 6), in addition to the Green River at Fort Dent (approximately river mile 11), which is about one river mile upstream of the Foster Links sampling location and upstream of the confluence with the Black River. Arsenic data[10] presented in the LDW RI included both surface water grab samples and composite samples, whereas the PAH and PCB data were grab samples only (as opposed to composite samples collected in this study)[11]. The data summarized in the LDW RI were collected between 2001 and 2008 during both storm and non-storm events (includes both wet and dry season non- storm samples). Statistical comparisons regarding

[10] The 2003 arsenic data summarized in the LDW RI are the same data evaluated in the Herrera 2005 study.

[11] The PCB grab samples collected for the LDW RI are not impacted by contamination from silicone tubing.

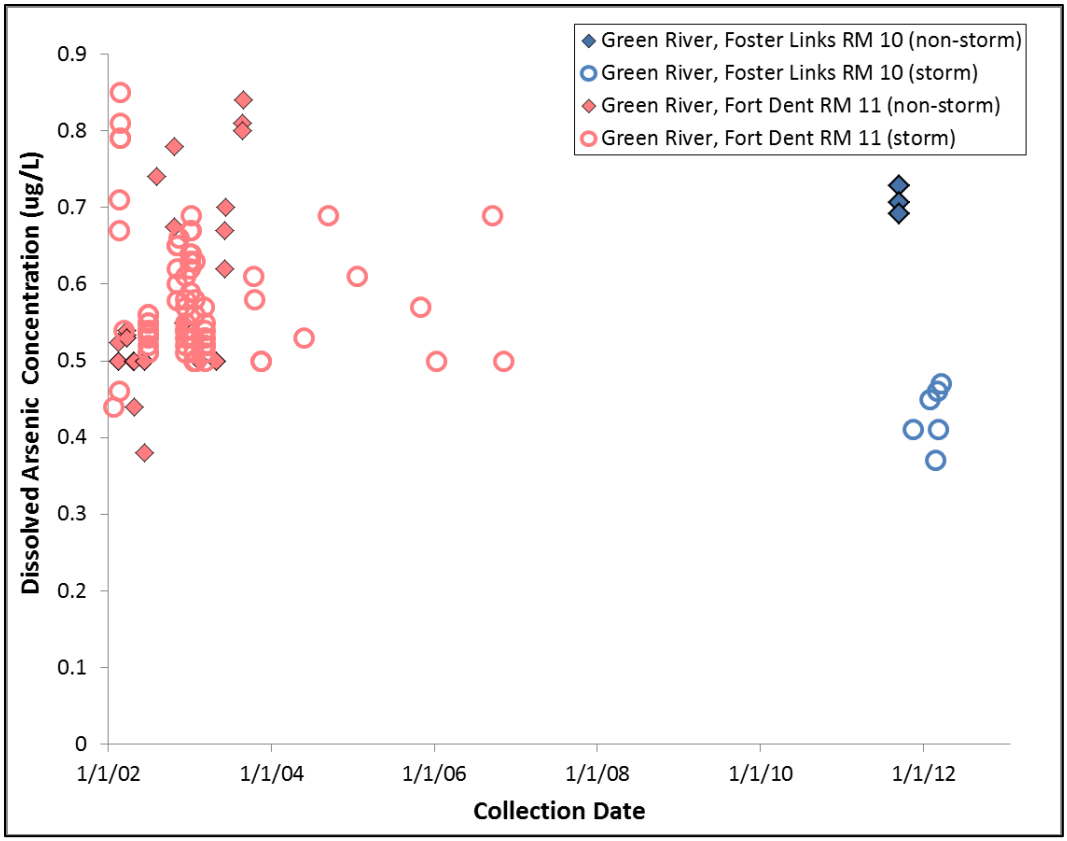
the differences between the previous and current studies were not made; therefore, only general observations of the data sets are discussed here.

While total arsenic concentrations for both data sets were within the same range (Figure 37), dissolved arsenic concentrations during storm events were generally lower in the current study. In addition, dissolved arsenic concentrations for non-storm events as presented by the LDW RI exhibited a larger concentration range than detected in the current study under baseflow conditions (Figure 38). When total LPAHs concentrations are compared, the current study showed a much wider range of concentrations during storm events, but a similar range during non-storm/baseflow events (Figure 39). HPAH results in the LDW RI indicate a broader range of concentrations during non-storm events compared to the current study, but a smaller range during storm events (Figure 40). However, for both LPAHs and HPAHs, the storm event data available for comparison is limited because data for only two storm events are presented in the LDW RI. Total PCB concentrations in the current study were within the range of the lowest LDW RI results for both storm and non-storm samples.



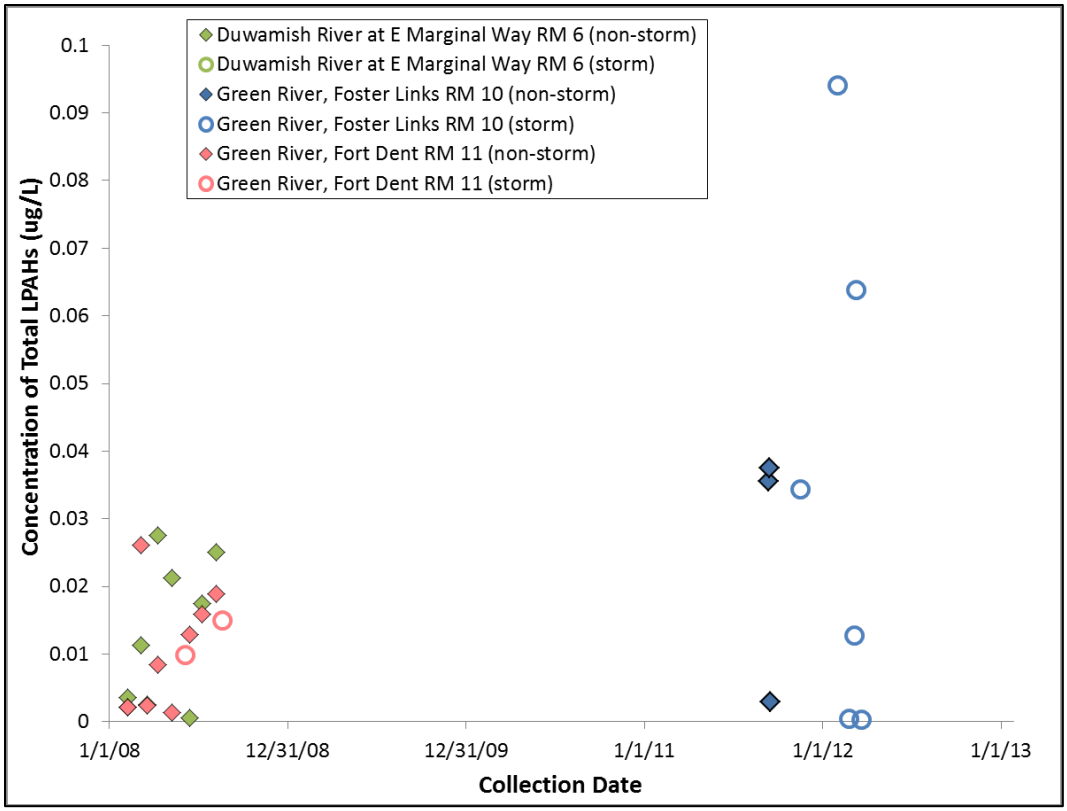
Mix of grab and composite samples collected from 2001 to 2008; 12-24 hour composite samples collected from 2011 to 2012. Foster Link samples are from the current study.

Figure 37. Total Arsenic Concentrations in Downstream Green River Grab and Composite Samples Collected Between 2001 and 2012



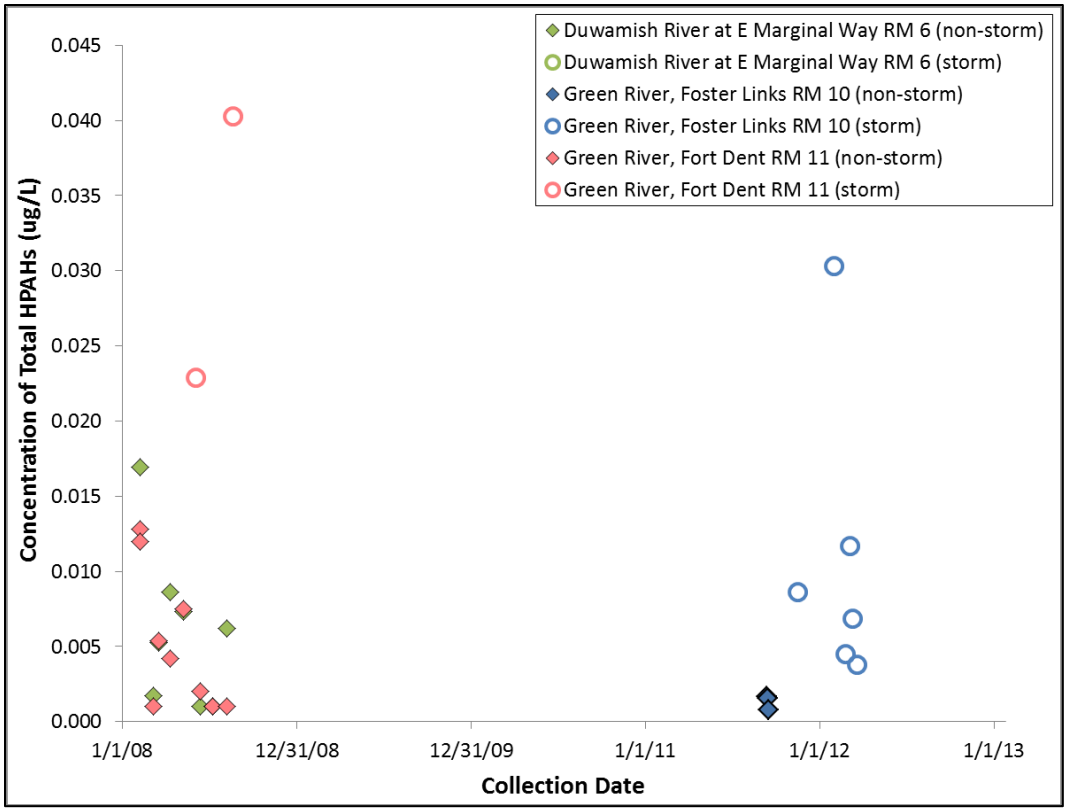
Mix of grab and composite samples collected from 2002 to 2008; 12-24 hour composite samples collected from 2011 to 2012. Foster Link samples are from the current study.

Figure 38. Dissolved Arsenic Concentrations in Downstream Green River Grab and Composite Samples Collected Between 2002 and 2012



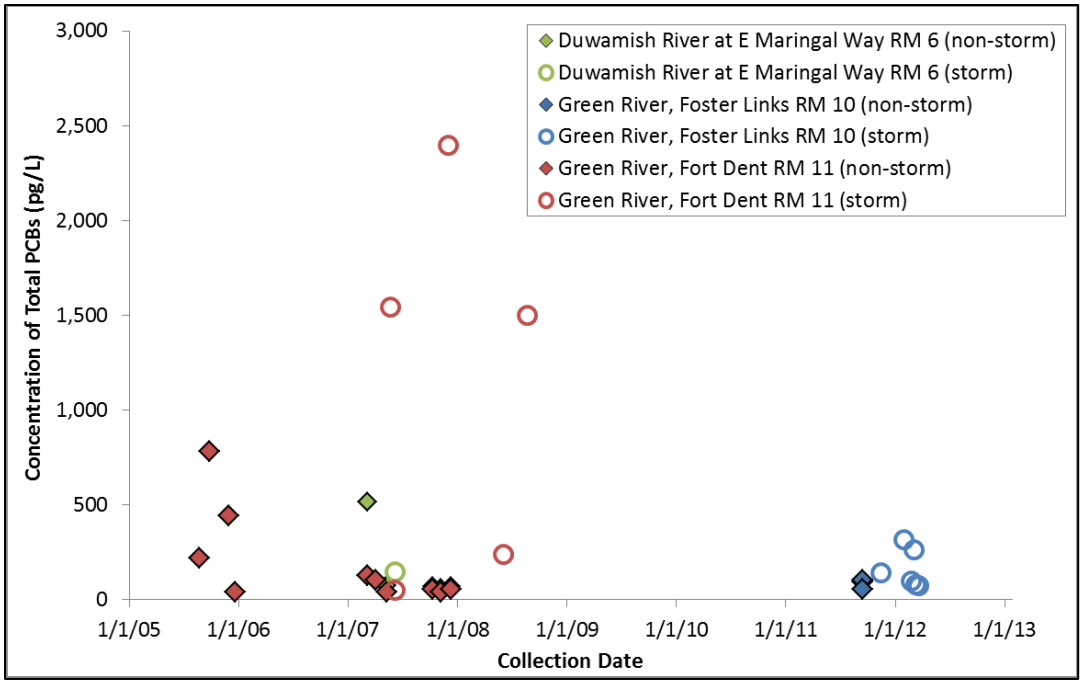
Grab samples collected in 2008; 12-24 hour composite samples collected from 2011 to 2012. Foster Link samples are from the current study.

Figure 39. Total LPAH Concentrations in Downstream Green River Grab and Composite Samples Collected Between 2008 and 2012



Grab samples collected in 2008; 12-24 hour composite samples collected from 2011 to 2012. Foster Link samples are from the current study.

Figure 40. Total HPAH Concentrations in Downstream Green River Grab and Composite Samples Collected Between 2008 and 2012



Grab samples collected from 2005 to 2008; 12-24 hour composite samples collected from 2011 to 2012. Foster Link samples are from the current study.

Figure 41. Total PCB Concentrations in Downstream Green River Grab and Composite Samples Collected Between 2005 and 2012

7.4 Comparison to Other Regional Watersheds

To provide additional context for interpretation, data from this study were compared to findings of the Surface Runoff Study conducted by Ecology (Ecology 2011) to evaluate chemical loadings from different land use types in the Puyallup and Snohomish watersheds. The purpose of this comparison was to evaluate if contaminant concentrations in the Green River and its major tributaries were similar to levels observed in two other large river systems in Western Washington.

The Ecology study collected both baseflow and storm event samples from multiple sub-basins representing a variety of land use types in both the Puyallup and Snohomish watersheds (Ecology 2011); samples were analyzed for a large suite of chemicals, including low level PAHs and PCB congeners. Unlike this Green River study where12-24 hour composite samples were collected, the Ecology study collected a single grab sample during baseflow conditions and generally two grabs (composited) during storm events. To facilitate data comparison, sampling locations from this study were classified by current land use, similar to the categorization used by the Ecology study. In addition, all sites regardless of land use type were combined; overall mean concentrations were generated for both baseflow and storm event conditions for each study for comparison purposes. Because no basins sampled in the Ecology Study were classified as mixed land use, the overall average of all Snohomish and Puyallup river sites combined was used to compare to Green River study locations classified as mixed land use (i.e., Mill Creek and the Green River at Foster Links). Total LPAH and HPAH concentrations are presented in Table 21, but are not discussed further due to low frequency of detection of individual PAH compounds in both studies.

Overall mean concentrations of total and dissolved arsenic were within about a factor of two between the studies. The overall mean of baseflow total PCBs were also similar between the studies (Table 21). When compared by land use type, most chemical concentrations were less than a factor of two between the studies, with a few exceptions. During baseflow conditions, dissolved arsenic concentrations in the largely residential and commercial basins, as well as total arsenic concentrations in residential basins were about three times greater on average in the Puyallup/Snohomish study. Also, PCB concentrations tended to be lower by landuse in the Green River study compared to the Puyallup/Snohomish study, with the exception of baseflow in commercial basins (Table 21). If the elevated PCB concentration in the one Soos Creek baseflow sample is not included, the average total PCB concentration including both Soos and Newaukum creeks of 123 pg/L would be similar to the residential basin average of 192 pg/L from the other two river systems.

Overall, this comparison suggests that arsenic and PCB concentrations in the Green River study area are generally within the range or lower than those detected in two other regional watersheds. In both studies, individual PAH detection frequencies were low. PAH detection limits for this Green River study were lower [12] and therefore more low level

[12] PAH Reporting limits ranged from 0.0097 to 0.034 µg/L in Ecology study compared to detection limits of 0.00014 to 0.00095 µg/L in this Green River Study.

detections were included in the LPAH and/or HPAH sums. This resulted in somewhat higher mean concentrations for some Green River study locations. Table 21 summarizes average chemical concentrations by study and basin type.

Table 21. Comparison of Mean Contaminant Concentrations in the Green River and its major tributaries to Other Regional River Basins

Study	Location	Number of Samples		Total Arsenic (µg/L)		Dissolved Arsenic (µg/L)		LPAHs (ug/L)		HPAHs (µg/L)		PCB (pg/L)	
		Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm	Base	Storm
Green River Averages (Current Study)	Green River – Flaming Geyser	3	6	0.804	0.54 J	0.797	0.42 J	0.010 J	0.048 J	n/d	0.0014 J	79.8 J	84.1 J
	Newaukum Creek[a]	3	6	0.647	0.50 J	0.641	0.47 J	0.012 J	0.024 J	n/d	0.0013 J	177 J	87.8 J
	Soos Creek[a]	3	6	1.05	0.682	1.00	0.58 J	0.054 J	0.030 J	n/d	0.0012 J	1,590 J	93.3 J
	Mill Creek	3	6	0.802	1.05	0.714	0.676	0.0082 J	0.051 J	0.00210 J	0.012 J	110 J	278 J
	Black River	3	6	0.838	0.868	0.49 J	0.60 J	0.019 J	0.037 J	0.0101 J	0.065 J	261 J	940 J
	Green River – Foster Links	3	6	0.966	0.964	0.709	0.43 J	0.025 J	0.034 J	0.0013 J	0.011 J	84.9 J	161 J
	Overall Average	-	-	0.851	0.77 J	0.73 J	0.53 J	**0.021 J**	**0.037 J**	0.0045 J	0.015 J	**384 J**	274 J
Puyallup & Snohomish Watershed Averages (Ecology 2009)	All Forested Basins	8	24 (12)	0.47	0.60	0.42	0.29	n/d	0.0071	n/d	n/d	181	207
	All Residential Basins	8	24 (12)	1.94	0.99	2.03	0.81	n/d	0.0085	n/d	0.0115	192	408
	All Commercial Basins	6	24 (12)	1.44	0.99	1.46	0.71	0.007	0.0238	0.0085	0.179	626	5714
	All Agricultural Basins	8	24 (4)	1.37	1.42	1.24	1.09	n/d	0.0071	n/d	0.0066	288	320
	Overall Average	-	-	**1.31**	**1.00**	**1.29**	**0.73**	0.007	0.0116	**0.0085**	**0.0657**	322	**1662**

Bolded values signify higher mean between studies. Sample numbers in parenthesis are for PCB analysis only. Ecology Study samples were a single grab for baseflow and up to two grabs for storm events; Green River study samples were 12-24 hr composite samples.
Light green shading signifies over 90% forested land use; yellow shading signifies over 50% residential and less than 10% commercial/industrial land use; pink shading signifies over 30% commercial/industrial land use; dark green shading signifies over 50% agriculture; dark grey shading signifies mixed land use.
[a] Greater than 45% residential land use. J = value estimated

7.5 Other Findings

While this study did not include a detailed assessment of the influence of significant water releases at the Howard Hansen dam on the parameters analyzed in this study, some general observations can be made. During the various sample collection periods, the largest water releases (>2,000 cfs) from the dam occurred on 1/31/2012 and 2/24/2012. Some of the highest TSS concentrations were detected in samples collected from the two Green River main stem locations on these dates; the highest total arsenic concentrations were also detected in samples from the Foster Links location on these dates. However, this pattern was not observed for the other parameters evaluated; there were no differences based on significant dam releases in dissolved arsenic or HPAH concentrations at either Green River location, or in total arsenic at the Flaming Geyser location. Total PCBs at the Flaming Geyser location tended to be lower during the storms with significant dam releases. There was no consistent pattern for TOC, DOC, and LPAHs at either Green River location, as well as total PCBs at the Foster Links location. These compounds were elevated during one of the two significant water release periods, but not during the other release period. These findings suggest that higher flow associated with dam releases does not always correspond with higher contaminant concentrations, although it may result in higher TSS. Inputs from local storm water runoff, in addition to the volume and intensity of rainfall must also be considered. In previous sampling efforts conducted during the LDW RI, a dry season storm event was captured (as opposed to the current study where storm events were collected only during the wet season). Total PCB concentrations detected during this dry season event were higher than in samples collected when Green River flows were elevated due to a dam release and no rainfall occurred (Windward 2010).

7.6 Key Findings, Current Sampling Efforts and Recommendations for Future Work

The major findings of this water quality study are presented below.

- Total PCB, LPAH, HPAH and TSS concentrations were generally greater during storm events than under baseflow conditions. Significant[13] differences between baseflow and storm event concentrations were observed at the Black River Pump Station for total PCBs, TSS, dissolved arsenic and HPAHs and at Newaukum, Soos, and Mill creeks combined for TSS. Dissolved arsenic differed in the tributaries where there were significantly higher concentrations during baseflow compared to storm events.

- During storm events, mean TOC and DOC concentrations were highest in Mill Creek, which were significantly higher than concentrations in the two main stem Green River locations. TSS concentrations during storm events were highest at the Green

[13] Use of the term "significant" refers to a statistically significant difference based on a statistical analysis.

River - Foster Links location, followed by Mill Creek; however, no significant differences were observed between any sites.

- During baseflow conditions, mean arsenic concentrations were within a factor of two at all sampling sites. During storm events, total and dissolved arsenic concentrations in Mill Creek were significantly higher than those detected in the two most upstream locations (Green River – Flaming Geyser and Newaukum Creek). During storm events, total arsenic concentrations in the Black River were also significantly greater than those in Newaukum Creek, as were dissolved arsenic concentrations in Mill Creek compared to the downstream Green River-Foster Links location.

- LPAH concentrations were variable across sites under both baseflow and storm event conditions and no significant differences were detected. Storm event HPAH concentrations were highest at the three most downstream locations: Mill Creek, Black River and the Green River - Foster Links location. During storm events, the highest HPAH concentrations were detected at the Black River Pump Station, which were significantly higher than concentrations measured at the three most upstream sites (Green River – Flaming Geyser, and Newaukum and Soos creeks).

- During storm events, total PCB concentrations were generally higher at the three most downstream locations: Mill Creek, Black River and the Green River - Foster Links location. PCB levels at the Black River Pump Station were significantly higher than at the Green River – Flaming Geyser site, Newaukum Creek, and Soos Creek. Under baseflow conditions, mean total PCB concentrations were highest in Soos Creek; however, elevated total PCB levels were detected in one sample and this data point greatly influenced the overall mean concentration.

- The highest concentrations of both total PCBs and total LPAHs were detected in a single baseflow sample collected from Soos Creek. Field observations at the time of sampling did not indicate any unusual conditions or elevated turbidity; however, TOC or DOC data are not available to provide additional context to help explain these findings. The laboratory QC analyses do not suggest that QC issues influenced this sample. PCBs and PAHs were analyzed by two different analytical laboratories, suggesting that these data were not influenced by laboratory error. Additional baseflow data collection would be necessary to evaluate whether these are anomalous concentrations.

- When storm event concentration data for the upstream and downstream Green River main stem locations were compared, significantly higher DOC, total arsenic and total HPAH concentrations were detected at the downstream location (Foster Links). No other significant differences were detected.

- Arsenic and total PCB concentrations in the Green River study area are within the range or lower than those observed in another study that included basins in the

Puyallup and Snohomish watersheds. In both studies, individual PAH detection frequencies were low.

- The comparison of sampling methods suggests that composite samples collected with the ISCO® autosampler deployed on the river bank are representative of conditions within the cross section of the Green River for all parameters except PCBs under baseflow conditions. The autosampler method yielded the higher PCB concentrations in both the baseflow and storm event sample pairs, with the most influential congeners including those indicative of contamination from silicone tubing (i.e., PCB-47, PCB-51, and PCB-68). After adjusting for the equipment contamination (see Section 5.6.1), storm event samples were comparable for the two methods, but baseflow samples still showed substantial differences, which could be due to environmental variability.

Collection of additional surface water data from the Green River Watershed is underway to further evaluate contaminant concentrations in the upper reaches of the Green River, both above and below the Howard Hanson Dam. Data collection from locations further upstream will provide additional water quality information from areas further removed from development and urbanization than the upstream Green River sampling location evaluated by this study (i.e., Flaming Geyser State Park). These data will allow King County to further characterize concentrations of target contaminants in areas less impacted by potential pollution sources. In addition, sample collection in the Green River during targeted storm events under periods of lower than average flow rates (e.g., during July-September) is recommended. Sample collection under these conditions will allow for further evaluation of local runoff when significant water releases from the Howard Hanson Dam are not occurring.

8.0. REFERENCES

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