Green River PCB Equipment Blank Study Data Report

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FINAL

King County

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EXECUTIVE SUMMARY

In 2014 and 2015, King County completed two surface water studies characterizing chemicals, including polychlorinated biphenyls (PCBs), in the Green River and its four major tributaries. These surface water characterizations support source control and cleanup of the Lower Duwamish Waterway (LDW) superfund site, as well as Ecology's Green-Duwamish Pollutant Loading Assessment. Based on previous method and equipment blank results, PCBs concentrations were found to be biased high in Green River water samples collected using ISCO® autosamplers; however, the degree of bias could not be estimated. This study aims to better understand the magnitude of equipment contamination bias associated with the Green River water sample PCB results, as well as to determine which equipment components contribute to the contamination. The study has two parts: field sampling and analysis of water samples from the Green River and analysis of laboratory collected equipment blank samples.

The field portion of this study consisted of autosampler composites and hand-grab composites collected concurrently at two Green River mainstem locations: Kanaskat-Palmer State Park and Foster Links Golf Course. Samples were collected from each site during three baseflow and three storm events using both sample methods (i.e., grab and autosampler). The contribution of PCBs by the autosampler equipment was evaluated by comparing PCB results between the sample pairs for each event and location. PCB concentrations in samples collected with the autosampler were consistently higher than levels in the concurrently collected hand-grab composite samples. PCB congeners PCB-47, PCB-51, and PCB-68 were the most prominent congeners in each autosampler composite (86% of total PCB concentrations on average), but were rarely detected in the concurrently collected hand-grab composite samples (5% of total PCB concentrations on average).

Laboratory equipment blank samples evaluated potential contamination associated with different types of tubing used for sample collection and processing. The findings indicate that use of standard silicone tubing results in a significant contribution of PCBs to environmental samples, specifically congeners PCB-47, PCB-51, and PCB-68. However, use of platinum-cured silicone tubing did not contribute to PCB sample contamination, while use of Teflon® tubing had a negligible contribution of PCBs in environmental samples.

Additional surface water samples collected from the Green River demonstrated that use of autosamplers with platinum-cured silicone and Teflon tubing collected representative PCB samples. The results showed negligible concentrations of the PCB congeners associated with equipment contamination (i.e. PCB-47, PCB-51, and PCB-68).

Based on the findings of this study, the 2014 and 2015 Green River surface water study reports have been revised to address the equipment contamination bias. Total PCB concentrations in these reports were adjusted to exclude the three PCB congeners affected by the standard silicone tubing (PCB-47, PCB-51, and PCB-68). This study indicates platinum-cured silicone tubing and Teflon tubing are acceptable for use in collection and processing of samples for PCB analysis.

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1.0 INTRODUCTION

This report presents the findings of the polychlorinated biphenyls (PCB) equipment blank study. The purpose of the study was to evaluate the potential for sampling equipment to cause contamination in samples analyzed for low-level PCBs, as well as to determine which equipment component was of concern. This study also provides an estimate of the bias the equipment contamination caused to Green River PCB surface water samples collected in previous King County studies (King County 2014; 2015a). Based on this study, data in two previous Green River data reports have been revised to include adjusted total PCB concentrations to better reflect environmental conditions without influence from equipment contamination (King County2018a, b).

1.1 Study Background

King County completed two surface water studies characterizing PCBs, polycyclic aromatic hydrocarbons, and arsenic in the Green River, as well as its the four major tributaries (King County 2014; 2015a). These efforts support Lower Duwamish Waterway (LDW) source control and cleanup of the superfund site. The data can also be useful for Ecology's Green-Duwamish Pollutant Loading Assessment (Ecology 2014). Water quality in the LDW is closely tied to water quality conditions in the Green River, which is the major source of water to the LDW. Based on previous method and equipment blank results, PCB concentrations were found to be biased high in Green River water samples collected using ISCO® autosamplers; however, the degree of bias could not be estimated (King County 2015a). This study aims to better understand the magnitude of equipment contamination bias associated with the Green River water sample PCB results, as well as to determine which equipment components contribute to the contamination.

1.2 Study Design

The study has two components: (1) field sampling and analysis of water samples collected at two locations in the Green River, and (2) analysis of laboratory blank samples collected using specific autosampler equipment tubing and sample splitting tubing. The study also generated additional PCB congener data for two previously sampled locations in the Green River.

The field sampling involved collection of whole surface water samples for analysis of PCB congeners at two locations in the Green River using two different sampling methods: autosamplers and composited hand-grabs. Concurrent sampling using these two different methods allows for direct comparison of PCB results and provides for an evaluation of bias from contamination associated with the autosampler equipment. Samples were collected during both wet season storm events and dry season baseflow conditions to better understand if the degree of equipment contamination differed based on river conditions. In addition, samples were collected from two previously sampled locations with differing landuse. The sampling locations were (1) "Kanaskat-Palmer" – the Green River at Kanaskat-Palmer State Park in the Middle Green River Basin where there is little development, and (2) "Foster Links" – the Green River at the Foster Links Golf Course in the Lower Green River Basin, which has substantially more upstream urban and suburban development. Both PCB congeners and conventional parameters, total organic carbon (TOC), dissolved organic carbon (DOC) and total suspended solids (TSS), were analyzed. The conventional parameter results assist in data interpretation, such as estimating particulate bound PCBs, as well as assessing natural variability at the site and comparability of the two sampling methods.

Silicone tubing has been associated with PCB congeners (Perdih and Jan 1994; Rodenburg 2015) and was suspected to be the source of the equipment-associated PCB contamination in previous Green River surface water samples (King County 2014; 2015a). Therefore, the study includes analysis of PCB congeners in laboratory water that was pumped through silicone tubing using the ISCO autosampler. To confirm that substantive PCB contamination is not originating from other tubing used for sample collection and processing, the study also includes testing of laboratory water that was passed through Teflon® tubing and tubing used to split samples in the laboratory. Equipment blank laboratory source water was also analyzed for PCBs as well. The analyses described here allow for an evaluation of potential PCB contamination from these materials.

The study design was amended after the project team became aware of a different grade of silicone tubing that might not be associated with PCB contamination: platinum-cured silicone tubing. Additional blank samples were collected using laboratory water pumped through the platinum-cured silicone tubing using the ISCO autosampler, as well as paired environmental samples using the each type of silicone tubing with autosamplers at the Foster Links location.

1.3 Report Organization

The remainder of this report summarizes the sampling and analytical methods as well as the data analysis methods (Section 2), an assessment of data quality (Section 3), study results (Section 4), and recommended adjustments to previously collected Green River water samples (Section 5). The analytical results as well as data validation reports are included in appendices to this report.

2.0 STUDY METHODS

The following section provides an overview of the sampling and analytical methods used in this study, as well as a summary of data analysis methods. The sampling procedures are described in detail in the sampling and analysis plan (SAP) and a memorandum from September 8, 2016 (King County 2015b and Williston 2016). Copies of completed chain of custody forms used to track sample custody are included in Appendix A.

2.1 Field Sampling

The SAP specified field sampling would consist of paired ISCO autosampler and composited hand-grab samples collected at Kanaskat-Palmer and Foster Links locations on the Green River mainstem (Table 1). Sampling at each of the two locations was conducted during three baseflow and three storm sampling events.

Table 1. Description of Sampling Locations

Locator	Locator Description	Approximate River Mile[a]	Northing[b]	Easting[b]
KP319	**Green River at Kanaskat-Palmer State Park** – west of day use shelters	52	119148	1373725
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.
[b] State plane coordinates in North American Datum 1983 (NAD83) Washington State Plane North (4601)

Paired time-weighted composite samples were collected over a 3-hour period. Each sampling method collected the same volume of water and the same number of aliquots (generally 10) over the same sampling period. The autosampler method followed the same procedures used during previous surface water sampling at these two locations. The autosampler was fitted with new, pre-cleaned, site-dedicated silicone tubing in the peristaltic pump for each sampling event. Site-dedicated Teflon tubing and stainless steel fittings were used for all other tubing needs. New Teflon tubing was used at the start of the project and was decontaminated prior to each sampling event. The water sample was split into sample analytical jars at the laboratory using the same type of splitting room tubing[1] as was used in past collection efforts. All hand-grab samples were collected using a proofed 1-liter glass jar and composited into a glass carboy in the field. The hand-grab composites were never exposed to silicone tubing, which was the expected source of PCB contamination. The hand-grab composite water sample was split into sample analytical jars at the laboratory using a vacuum system instead of a peristaltic pump. Only Teflon tubing was used for the vacuum splitting method. Two field replicates were collected at Foster Links. Table 2 summarizes the paired samples and field replicates collected, including flow and rainfall conditions for each sampling event.

[1] When samples are received in the laboratory, aliquots are drawn from the autosampler carboy and placed into the appropriate analytical containers. This is accomplished with a peristaltic pump and Teflon/silicone/Teflon tubing combination that has been decontaminated between uses.

Table 2. Summary of sampling events for paired collection methods: autosampler composites with standard silicone tubing and hand-grab composites.

Site	Flow Condition	Start Time	Time-span (hours)	Average Flow [a] (cfs)	Rainfall During Sampling (inches)	Rainfall 12 Hours Prior (inches)	Samples Collected
Kanaskat-Palmer	Baseflow	06/24/15 11:40	3	227	0.00	0.00	L63070-1 and -2
		08/20/15 9:47	3	198	0.00	0.00	L63208-1 and -2
		09/29/15 10:20	3	391	0.00	0.00	L63826-1 and -2
	Storm	04/14/15 12:00	3	463[a]	0.00	0.03[b]	L62563-1 and -2
		10/07/15 12:30	3	456	0.12	0.30	L62766-1 and -2
		10/30/15 11:00	3	581	0.01	0.29	L64061-1 and -2
Foster Links	Baseflow	06/24/15 12:09	3	303	0.00	0.00	L63069-1 and -2
		08/20/15 11:28	3	264	0.00	0.01	L63207-1 and -2
		10/01/15 10:30	3	427	0.00	0.00	L63825-1, -2, -3, and -4
	Storm	10/31/15 11:30	3	2,029	0.13	1.18	L62562-1 and -2
		12/07/15 11:20	3	1,682	0.42	0.35	L64136-1 and -2
		12/21/15 11:40	3	2,681	0.35	0.41	L64454-1, -2, -3, and -4

[a] Average flow is the average of hourly flow readings over the sampling period, except for the 04/14/15 storm at Kanaskat-Palmer where only average daily flow was available.
[b] The 24-hour rainfall prior to sampling was 0.58 inches.

Based on PCB results of the paired field samples and laboratory equipment blank samples, additional field sampling was conducted at Foster Links over two storm events (Table 3). This sampling was conducted to compare PCB concentrations in paired ISCO autosampler composites collected with new, pre-cleaned standard silicone tubing and new, pre-cleaned platinum-cured silicone tubing (Williston 2016). Samples were split using new, pre-cleaned silicone tubing matching the types used for the sample collection. New Teflon tubing was used at the beginning of the project, site-dedicated, and decontaminated prior to each sample collection.

All surface water samples were analyzed for PCB congeners, TSS, TOC, and DOC. Four samples were also analyzed for arsenic and polycyclic aromatic hydrocarbons.

Table 3. Summary of sampling events for paired collection methods: autosampler composites with standard silicone tubing and platinum-cured silicone tubing.

Site	Flow Condition	Start Time	Time-span (hours)	Average Flow [a] (cfs)	Rainfall During Sampling (inches)	Rainfall 12 Hours Prior (inches)	Samples Collected
Foster Links	Storm	05/04/17 18:00	6	625	0.33	0.30	L67711-1 and -2
		05/12/17 12:45	12	605	0.10	0.06	L67737-1 and -2

[a] Average flow is the average of hourly flow readings over the sampling period.

2.2 Equipment Sampling

King County Environmental Laboratory (KCEL) reverse osmosis (RO) water was passed through different types of tubing and analyzed for PCB congeners. The testing was designed to isolate each type of tubing used in sampling and processing of environmental samples. The sampling procedure details followed for these equipment blank samples are presented in the SAP. Laboratory RO water was also transferred from the KCEL system directly to 1-liter glass containers for PCB analysis. Following the start of this study, King County became aware of platinum-cured silicone tubing as an alternative to the standard silicone tubing. The platinum-cured tubing is manufactured in a way that does not form PCB byproducts that can leach from the silicone (i.e., through the curing process). Therefore, additional equipment testing was added that included this type of silicone tubing. A list of all analyzed equipment blank samples is provided in Table 4.

Table 4. Equipment Blank Sample Types

Equipment	Sample ID	Sample Description
RO water	L63330-4	Collected directly from tap at main sink in splitting room, no silicone tubing on spout
RO water	L63543-4	Collected directly from the sink in Virology lab in Microbiology unit, no silicone tubing on spout
RO water	L65645-1	Collected directly from tap at main sink in splitting room, no silicone tubing on the spout
Standard silicone tubing	L63330-1	Composite of RO water via autosampler over 8-hour period through 6 feet of new, pre-cleaned silicone tubing (Versilic SPX-5). Same set-up used for sample splitting, no Teflon.
Standard silicone tubing	L63543-1	Composite of RO water via autosampler over 7-hour period through 6 feet of new, pre-cleaned silicone tubing (Versilic SPX-5). Same set-up used for sample splitting, no Teflon.
Standard silicone tubing	L67549-1	Composite of RO water via autosampler over 23-hour period through 6 feet of new, pre-cleaned silicone tubing (Versilic SPX-5). Same set-up used for sample splitting, no Teflon.
Teflon tubing	L63330-2	Transferred 10 liters of RO water five times between two 5-gallon carboys, 20 feet of new, pre-cleaned Teflon tubing. Same set-up used for sample splitting, no silicone.

Equipment	Sample ID	Sample Description
Teflon tubing	L63543-2	Transferred 12 liters of RO water five times between two 5-gallon carboys, 20 feet of pre-cleaned Teflon tubing (previously used to collect sample L63330-2). Same set-up used for sample splitting, no silicone.
Teflon tubing	L66603-1	Transferred 12 liters of RO water five times between two 5-gallon carboys, 25 feet of pre-cleaned Teflon tubing (previously used to collect samples L63330-2 and L63543-2). Same set-up used for sample splitting, no silicone.
Splitting room tubing	L63330-3	Sample containers were filled with RO water using peristaltic pump. Used 6 feet of pre-cleaned, previously used silicone pump tubing (Versilic SPX-5) with two 24-inch pre-cleaned, previously used Teflon tubes attached.
Splitting room tubing	L63543-3	Sample containers were filled with RO water using peristaltic pump. Used 6 feet of pre-cleaned, previously used silicone pump tubing (Versilic SPX-5) with two 24-inch pre-cleaned, previously used Teflon tubes attached
Platinum-cured silicone tubing	L63772-1	Composite of RO water via autosampler over 7-hour period through 6 feet of new, pre-cleaned platinum-cured silicone tubing (Cole-Parmer, PN 96440-73). Same set-up used for sample splitting, no Teflon.
Platinum-cured silicone tubing	L63772-2	Composite of RO water via autosampler over 7-hour period through 6 feet of new, pre-cleaned platinum-cured silicone tubing (Cole-Parmer, PN 96410-73). Same set-up used for sample splitting, no Teflon.
Platinum-cured silicone tubing	L64487-1	Composite of RO water via autosampler over 23-hour period through 6 feet of new, pre-cleaned platinum-cured silicone tubing (Cole-Parmer, PN 96410-73). Same set-up used for sample splitting, no Teflon.

2.3 Laboratory Methods

The laboratory analyses performed for this study included PCB congeners and conventional analyses for TOC, DOC and TSS. PCB congener analysis was conducted by Pacific Rim Laboratories (PRL) and AXYS Analytical Services, Ltd. (AXYS). Conventional parameters were analyzed by the KCEL.

The KCEL reports both the reporting detection limit (RDL) and the method detection limit (MDL) for each sample and parameter. 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, laboratory blank contamination. Thus, PCB congener data are reported to lowest method calibration limits (also referred to as estimated quantitation limit (EQL) by some laboratories) and flagged as estimated down to the sample-specific detection limit (SDL) value. The following sections provide a summary of the laboratory methods; greater detail can be found in the project SAP (King County 2015b).

2.3.1 PCB Congeners

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

PRL performed PCB analysis according to their SOP LAB02 using an SGE HT-8 column. A one-liter sample is extracted followed by standard method cleanup, which includes an acid wash followed by Acid Silica and Alumina column chromatography.

AXYS performed PCB analysis according to their SOP MLA-010 Analytical Method for the Determination of 209 PCB Congeners by EPA Method 1668 using an SPB Octyl column and a secondary DB1 column to resolve the co-eluting congeners PCB156 and PCB157. A one-liter sample was extracted followed by standard method cleanup, which includes layered Acid/Base Silica, Florisil, and Alumina.

Some of the key differences between the two laboratories are the analytical columns used and the sample-specific detection level reported for many congeners. Both columns are acceptable for the method with the main difference being the pattern of co-eluting congeners. Co-eluting congeners move through an analytical column at the same rate and cannot be quantified in isolation. Results are presented as the sum of the coeluting congeners. The SGE HT-8 column results in fewer co-eluting congeners than the SPB Octyl column, allowing for quantification of a greater number of individual congeners.

2.3.2 Conventional Water Quality Parameters

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

2.4 Deviations from the SAP

There were no analytical and field method deviations from the SAP.

2.5 Data Analysis Methods

The treatment of the PCB congener and conventional parameter data prior to data analysis is presented here.

2.5.1 Flagged and Non-detect Results

PCB congeners flagged as "non-detect" by the laboratory or data validation are not included in total PCB sums, while those flagged as estimates are included in total PCB sums. Total

PCBs for almost all samples include at least one congener flagged as an estimate; therefore, most total PCB concentrations are flagged as estimates. However, one sample (and the associated field replicate) had no PCB congener detections following data validation. For these samples, the value of the highest SDL for an individual congener was used to represent the level of detection and the value used for data analysis.

2.5.2 Significant Figures

Conventional parameter data generated by the KCEL are reported to three significant figures, unless the value is below the RDL. In these cases, the value has higher uncertainty and is reported to only two significant figures. PRL and AXYS report PCB congener results to three significant figures. Therefore, when calculating total PCBs from the congener results, the total was rounded to three significant figures.

2.5.3 Laboratory Duplicates and Field Replicates

Laboratory duplicates and field replicates were used to assess analytical and field sampling variability, but only primary sample results were included in the analyses presented in the report. Section 3.0 describes data quality assessments, including evaluation of laboratory duplicate and field replicate results.

2.5.4 Data Presentations

Data presentations illustrate PCB congener concentrations for individual samples or average concentrations. Congeners are identified by International Union of Pure and Applied Chemistry (IUPAC) numbers. When average concentrations were calculated for individual congeners, a value of zero was used for non-detect results. The figures in Section 4 present all detected PCB congeners. Coeluting congener concentrations are identified on the x-axis by the IUPAC number of the first coeluting congener followed by a “c” (e.g., 47c).

3.0 DATA QUALITY ASSESSMENT

The project SAP (King County 2015b) describes the data quality objectives for the project. Representativeness, completeness, comparability, and sensitivity objectives were met as described in the SAP. Precision, accuracy, and bias were assessed through analysis of a variety of laboratory quality control (QC) samples and field replicates. This section provides a summary of the data validation findings, a comparison of field replicate results, and discusses how laboratory and environmental variability need to be considered during interpretation of the study results.

3.1 Data Validation Summary

The KCEL QC results for TSS, TOC, and DOC indicated samples met quality requirements for all but four DOC samples. These samples were flagged as estimates due to filtering outside of hold time requirements. Overall, the data demonstrated acceptable quality for study use, with no rejected results. Appendix B includes the data validation memorandum and associated QC data for the parameter data generated by the KCEL.

PCB data were validated to Level III by Laboratory Data Consultants, Inc. (LDC) in accordance with EPA Region 10 guidance (EPA 1995). 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. PCB congener validation reports are provided in Appendix B[2].

PCB samples were analyzed in six batches by PRLs and two batches by AXYS. No results were rejected based on data validation; however, a number of individual congener results were qualified as estimated (J flagged) or not-detected (U flagged) based on various data quality results. A summary of reasons for data qualifiers is presented below.

- Due to internal standard percent recovery exceeding QC limits, 11 congeners in one sample were qualified as estimated.
- Due to laboratory control sample recoveries below QC limits, 3 congeners (including one co-eluting pair) in 11 samples were qualified as estimated.
- Due to initial calibration percent relative standard deviation exceeding QC limit, 36 congeners (including 6 co-eluting pairs) were qualified as estimated in two samples.
- Due to laboratory control sample recoveries below QC limits, 5 congeners were qualified as estimated in two samples.

[2] Samples L64136-1 and -2 were analyzed twice, and therefore, are included in two validation reports. The first sample results showed the PCB congeners of interest for silicone tubing were ‘N” flagged (estimated maximum possible concentration) by PRL because not all identification and qualification criteria were met for these compounds. In these cases, congener data are qualified as not detected by data validator, and thus, are not useful to evaluate the study questions. When the archive samples were analyzed, the congeners of interest were quantified without the ‘N’ flag qualifier.

- Due to continuing calibration percent recovery exceeding QC limit for 3 labeled compounds and below QC limit for one labeled compound, 27 congeners (including one co-eluting pair) were qualified as estimated in one sample.
- Due to laboratory duplicate relative percent difference (RPD) exceeding QC limit, one congener was qualified as estimated in one sample.

The lowest detected PCB method blank contaminant was PCB-187 (0.538 pg/L) for work group WG51112. The highest detected PCB congener in method blanks was PCB-11 (38.4 pg/L) in workgroup WG53482. Total PCBs detected in method blanks ranged from 14.9 to 131 pg/L. Environmental sample congener detections were qualified as non-detect whenever congener concentrations were less than five times the method blank concentration for that work group. This resulted in some congener data being qualified as not detected in 45 samples.

The analytical laboratory qualified numerous PCB congeners as “K” (AXYS) or “N” (PRL), indicating that not all identification and qualification criteria were met for these compounds. The maximum potential concentration is reported for “K” or “N” flagged congeners. These analytes were qualified as non-detects (U qualified) based on EPA Region 10 validation requirements.

3.2 Field Replicates

There is an accepted level of uncertainty in analytical results, as defined by analytical QC limits (e.g., 50% RPD between laboratory duplicate results for individual PCB congeners[3]). Additionally, results below reporting limits (i.e., RDLs for conventional parameters and EQLs for PCB congeners) are considered estimated values due to known uncertainties in quantifying concentrations below these levels. This type of analytical uncertainty plays a factor in data interpretation for this study.

There are also sources of uncertainty from environmental factors. Field replicates were used to assess environmental variability of the sampled matrix. The conventional parameters showed little environmental variability, with results well within acceptable analytical variability (i.e., 25% RPD for TSS and 20% RPD for TOC/DOC)[4] (Table 5). Table 6 lists paired sample results for all PCB congeners detected in one or both samples. The table compares detected results by reporting the RPD. Congeners detected below the EQL were frequently not detected in the paired sample, although the SDLs for the non-detect values were often comparable to the detections in the paired sample (Table 6). Detections greater than the EQL were almost always shared between paired samples, indicating consistent identification of prominent PCB congeners. However, RPDs between detected results

[3] RPDs are only calculated when both the laboratory duplicate and primary sample results are greater than the EQL.

[4] The analytical QC limits for laboratory duplicates are used as a benchmark for assessing differences in results throughout the report. While analytical QC limits are not intended for evaluating precision outside the laboratory, they can provide a sense of how influential outside factors may be to results compared to the acceptable level of analytical variability.

ranged from 10% to 93%, indicating greater environmental variability for PCB results when compared to conventional parameter results (Table 5).

Table 5. Comparison of conventional parameter results between primary samples and field replicates.

Site	Flow Condition	Parameter	Autosampler Composite			Hand-Grab Composite		
			Primary Sample (mg/L)	Field Replicate (mg/L)	RPD	Primary Sample (mg/L)	Field Replicate (mg/L)	RPD
Foster Links	Baseflow	TSS	2.63	2.80	6%	2.80	2.74	2%
		TOC	1.53	1.58	3%	1.32	1.47	11%
		DOC	1.4	1.54	10%	1.28	1.29	1%
	Storm	TSS	15.4	14.8	4%	13.5	13.6	1%
		TOC	2.75	2.55	8%	2.44	2.40	2%
		DOC	2.39	2.34	2%	2.27	2.20	3%

Table 6. Comparison of detected PCB congener results between primary samples and field replicates as analyzed by PRL.

Site	Flow Condition	Sampling Method	IUPAC #	Primary Sample (pg/L)	Field Replicate (pg/L)	RPD
Foster Links	Baseflow 10/01/15	Autosampler Composite	18	9.97 J	<6.68 UJ	NC
			47c	167	96.0	54%
			68	139	119	16%
			95	13.0 J	<15.9 UJ	NC
			153	1.36 J	<1.58 UJ	NC
		Hand-Grab Composite	No congeners detected.			
	Storm 12/21/15	Autosampler Composite	2	6.98 J	<0.898 UJ	NC
			3	7.12 J	<1.19 UJ	NC
			17	15.9 J	<6.77 UJ	NC
			18	10.1 J	<5.01 UJ	NC
			32	25.0	<8.00 UJ	NC
			47c	122	110	10%
			51	141	51.6	93%
			68	186	76.5	83%
		Hand-Grab Composite	1	<3.68 U	1.64 J	NC
			17	<20.8 U	10.3 J	NC
			31	<5.60 UJ	5.56 J	NC
			50	15.5 J	3.47 UJ	NC
			105c	<16.0 UJ	13.7 J	NC
			141	<0.777 UJ	2.79 J	NC

J – estimated value (below EQL); UJ – estimated non-detect; U – non-detect;
<## – not detected at sample detection limit; NC – not calculated because of non-detect value

3.3 Data Quality Summary

The data quality objectives were achieved and thus the study questions can be assessed. When comparing results to address the study questions, analytical and environmental variability should be considered. Slight variations between results may be due to laboratory and/or environmental variability; however, substantial and consistent differences between results above RDLs or EQLs can more confidently be attributed to study variables.

4.0 STUDY RESULTS

Three groups of data were collected for this study: (1) paired environmental samples to compare results collected with the hand-grab composite and autosampler composite methods, (2) blank samples to identify the equipment likely responsible for PCB sample contamination, and (3) paired environmental samples to compare results collected with standard silicone tubing and platinum-cured silicone tubing. This section presents and discusses these data. All validated results associated with this project are included as Appendix C. The analytical methods and results of the Green River surface water samples analyzed for arsenic and polycyclic aromatic hydrocarbons are only presented in Appendix D, because these data were not the focus of this study.

4.1 Hand-Grab Composites versus Autosampler Composites

Results were compared between hand-grab composite samples and concurrently collected autosampler composite samples from two sites on the Green River mainstem (Kanaskat-Palmer and Foster Links). As discussed in Section 2.1, the main difference between the sampling methods was use of standard silicone tubing with the autosampler collections and the sample splitting process. All samples were analyzed by PRL. However, two paired samples (L62563-1 and 2; L64454-1 and -2) were also analyzed by AXYS, which was the laboratory that analyzed the previous Green River studies' samples. The analyses conducted by AXYS were originally intended to confirm that differences between the laboratories' analytical columns and sensitivities would not affect the outcome of how to adjust concentrations measured in the previous Green River studies' samples. Using two different analytical columns also assisted in confirmation of which specific congeners were of concern for the equipment contamination.

4.1.1 Conventional Parameters

Conventional parameter results were very similar between sampling methods (Tables 7 and 8). With the exception of TSS results in two sample pairs, concentrations were similar and RPDs were within analytical QC limits for each method. The relative differences in conventional parameter results are comparable to laboratory and environmental variability, as discussed in Section 3. If the conventional parameter results had been substantially different between the methods, it would have suggested site conditions were extremely variable. This has implications for comparing PCB results between sampling methods, because substantially variable site conditions could mask differences in PCB results attributable to sampling equipment differences. Instead, the relatively similar conventional parameter results between methods indicate the two sampling methods are comparable to assess PCB differences due to sampling equipment.

Table 7. Baseflow conventional parameter results by sampling method for each site.

Site	Parameter	Date	Parameter Concentration (mg/L)		RPD
			Autosampler Composite	Hand-Grab Composite	
Kanaskat-Palmer	TSS	06/24/15	1.20	1.0 J	18%
		08/20/15	1.38	0.96 J	NC
		09/29/15	3.16	2.74	14%
	TOC	06/24/15	1.08	0.96 J	12%
		08/20/15	1.05	1.07	2%
		09/29/15	1.72	1.55	10%
	DOC	06/24/15	0.80 J	0.78 J	3%
		08/20/15	0.95 J	0.98 J	3%
		09/29/15	1.17 J	1.08 J	8%
Foster Links	TSS	06/24/15	3.70	3.20	14%
		08/20/15	3.12	4.70	40%
		10/01/15	2.63	2.80	6%
	TOC	06/24/15	2.38	1.95	20%
		08/20/15	2.05	2.17	6%
		10/01/15	1.53	1.32	15%
	DOC	06/24/15	1.64	1.76	7%
		08/20/15	1.80	1.53	16%
		10/01/15	1.40	1.28	9%

J – estimated value; NC – RPDs were not calculated from estimated values

Table 8. Storm event conventional parameter results by sampling method for each site.

Site	Parameter	Date	Parameter Concentration (mg/L)		RPD
			Autosampler Composite	Hand-Grab Composite	
Kanaskat-Palmer	TSS	04/14/15	1.70	1.58	7%
		10/07/15	2.95	3.26	10%
		10/30/15	2.90	6.00	70%
	TOC	04/14/15	1.27	1.08	16%
		10/07/15	1.84	1.79	3%
		10/30/15	1.17	1.25	7%
	DOC	04/14/15	1.03	0.77 J	NC
		10/07/15	1.80	1.70	6%
		10/30/15	1.13	1.02	10%
Foster Links	TSS	10/31/15	32.6	30.6	6%
		12/07/15	25.2	24.4	3%
		12/21/15	15.4	13.5	13%

Site	Parameter	Date	Parameter Concentration (mg/L)		RPD
			Autosampler Composite	Hand-Grab Composite	
	TOC	10/31/15	3.04	2.77	9%
		12/07/15	4.53	3.94	14%
		12/21/15	2.75	2.44	12%
	DOC	10/31/15	2.72 J	2.60 J	5%
		12/07/15	3.96	3.82	4%
		12/21/15	2.39	2.27	5%

J – estimated value; NC – RPDs were not calculated from estimated values

4.1.2 Pacific Rim Laboratory PCB Congener Results

Total PCB concentrations in the autosampler composites were consistently and substantially higher than in the hand-grab composites (Table 9). Total PCB concentrations in the autosampler composites were dominated by three congener groups (i.e., PCB-47/48, PCB-51, and PCB-68), while concentrations of these congeners were negligible in the hand-grab composites (Table 10; Figures 1 and 2[5]). The magnitude and consistency of these differences indicate PCB contamination was associated with the autosampler method rather than the result of laboratory or environmental variability.

Table 9. Comparison of total PCB results by sampling method for each sample pair.

Site	Flow Condition	Date	Total PCBs (pg/L)	
			Autosampler Composite	Hand-Grab Composite
Kanaskat-Palmer	Baseflow	06/24/15	594 J	25.0 J
		08/20/15	561 J	47.8 J
		09/29/15	193 J	40.1 J
	Storm	04/14/15	383 J	51.4 J
		10/07/15	317 J	14.8 J
		10/30/15	297 J	23.0 J
Foster Links	Baseflow	06/24/15	434 J	109 J
		08/20/15	523 J	25.5 J
		10/01/15	330 J	10.3 U
	Storm	10/31/15	384 J	53.5 J
		12/07/15	396 J	211 J
		12/21/15	514 J	15.5 J

J – estimated sum; U – non-detect at highest congener SDL

[5] These figures demonstrate the variability in low-level detections of PCB congeners (<EQL [about 20 pg/L]), as described in Section 3.2. This low-level variability does not obscure the substantial and consistent differences in concentrations of PCB-47/48, PCB-51, and PCB-68 between the sampling methods.

Table 10. Comparison of average contribution of suspect PCB congeners to total PCB concentrations by sampling method for each site and flow condition.

Site	Flow Condition	Average % of Total Contributed from PCB-47/48, PCB-51, and PCB-68	
		Autosampler Composite	Hand-Grab Composite
Kanaskat-Palmer	Baseflow	95%	0%
	Storm	92%	5%
Foster Links	Baseflow	87%	3%
	Storm	70%	5%

Adjusting total PCB concentrations to exclude these suspect congeners resulted in less variability in concentrations between sampling methods for most events (Table 11); however, analytical and environmental variability are still present (See Section 3).

Table 11. Comparison of total PCB results excluding suspect congeners for each sample pair.

Site	Flow Condition	Date	Adjusted Total PCBs (pg/L)[a]	
			Autosampler Composite	Hand-Grab Composite
Kanaskat-Palmer	Baseflow	06/24/15	30.9 J	25.0 J
		08/20/15	23.3 J	47.8 J
		09/29/15	12.2 J	40.1 J
	Storm	04/14/15	50.8 J	51.4 J
		10/07/15	15.1 J	14.8 J
		10/30/15	18.2 J	18.2 J
Foster Links	Baseflow	06/24/15	74.1 J	109 J
		08/20/15	67.3 J	21.4 J
		10/01/15	24.3 J	9.49 J
	Storm	10/31/15	104 J	42.8 J
		12/07/15	221 J	209 J
		12/21/15	65.1 J	15.5 J

[a] Total PCB concentrations excluding PCB-47/48, PCB-51, and PCB-68.
J – estimated sum

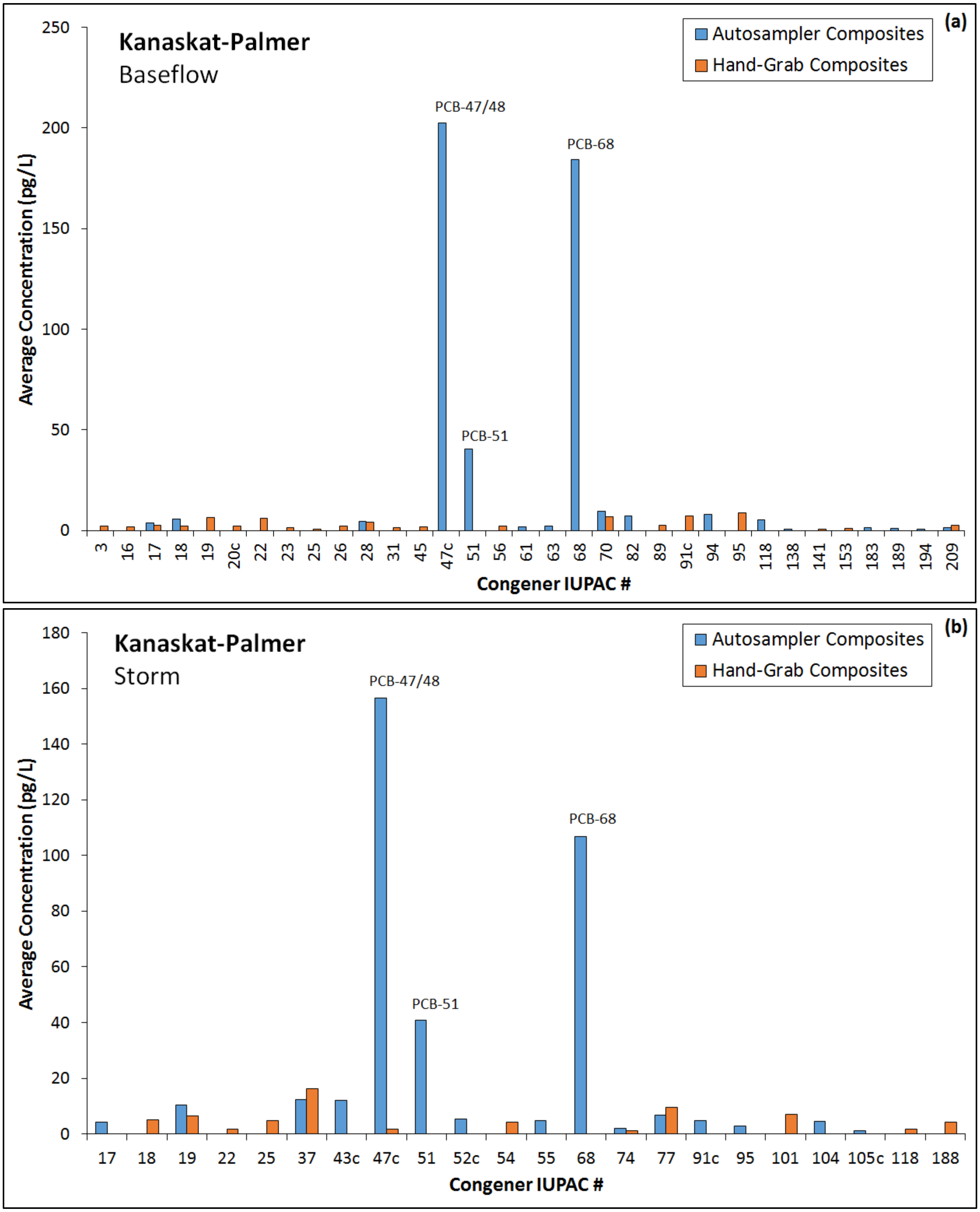


Figure 1. Average PCB Congener Concentrations by Sampling Method at Kanaskat-Palmer for: (a) Baseflow, (b) Storm

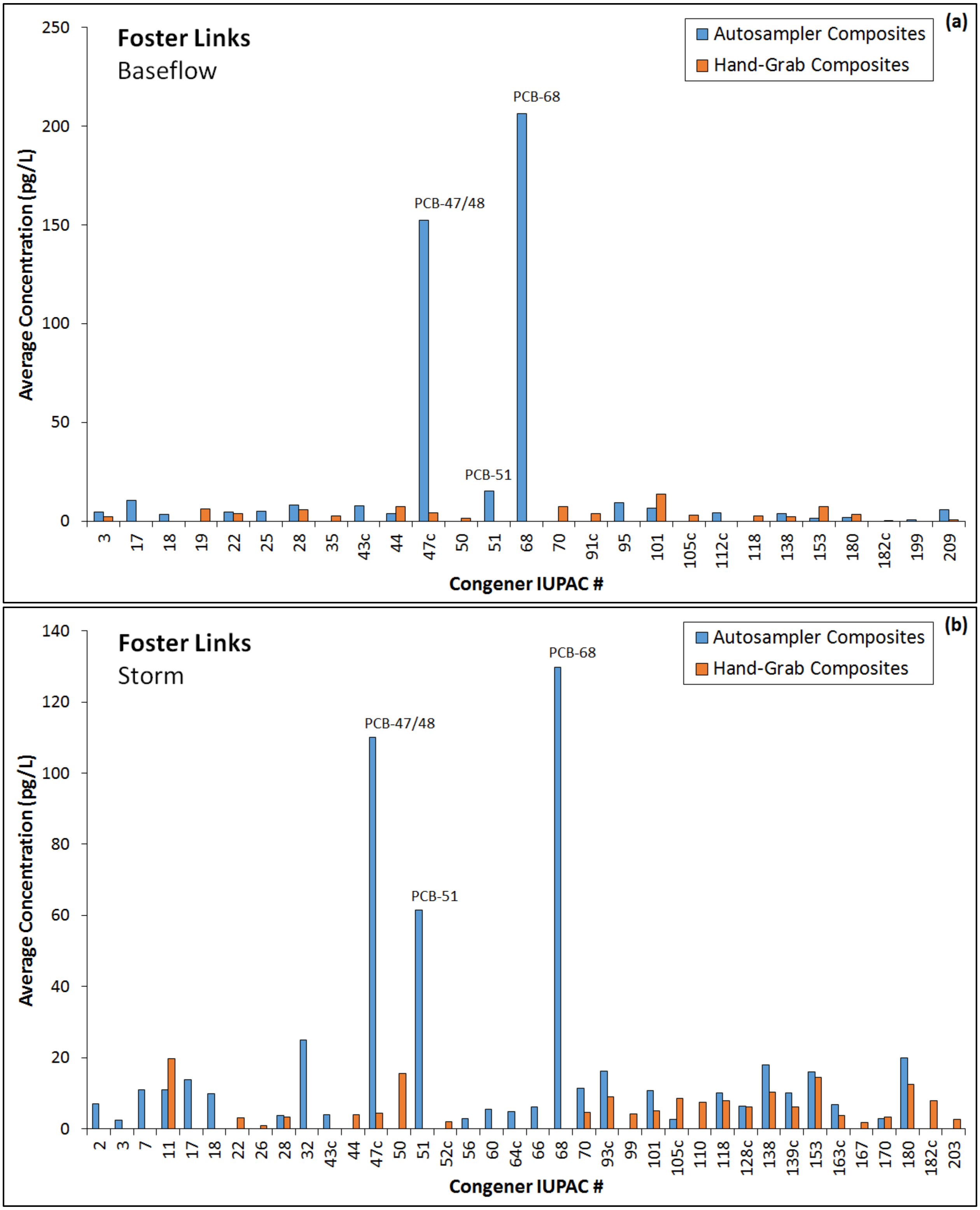


Figure 2. Average PCB Congener Concentrations by Sampling Method at Foster Links for: (a) Baseflow, (b) Storm

4.1.3 AXYS Analytical PCB Congener Results

Two sets of storm event samples, one at each Green River sampling location, were also analyzed by AXYS. As with the PRL results, total PCB concentrations were much higher in the autosampler composites compared to the hand-grab composites. As before, the contributions from a few congeners (PCB-44/47/65, PCB-45/51, and PCB-68) dominated the total PCB concentrations in samples collected with the autosampler, but were negligible in hand-grab composites (Figures 3 and 4). These data confirmed that the findings were not unique to a given analytical laboratory (Table 12).

As noted earlier, some PCB congeners cannot be quantified in isolation, because they coelute with other congeners during analysis. The specific analytical column used by the laboratory dictates which congeners co-elute. In comparing sample results for PRL and AXYS for the same event, contributions from individual congeners can be isolated. The individual congeners PCB-47, PCB-51, and PCB-68 were identified as the influential congeners from the autosampler method by comparing results between these two laboratories (e.g., Figure 1a versus Figure 3).

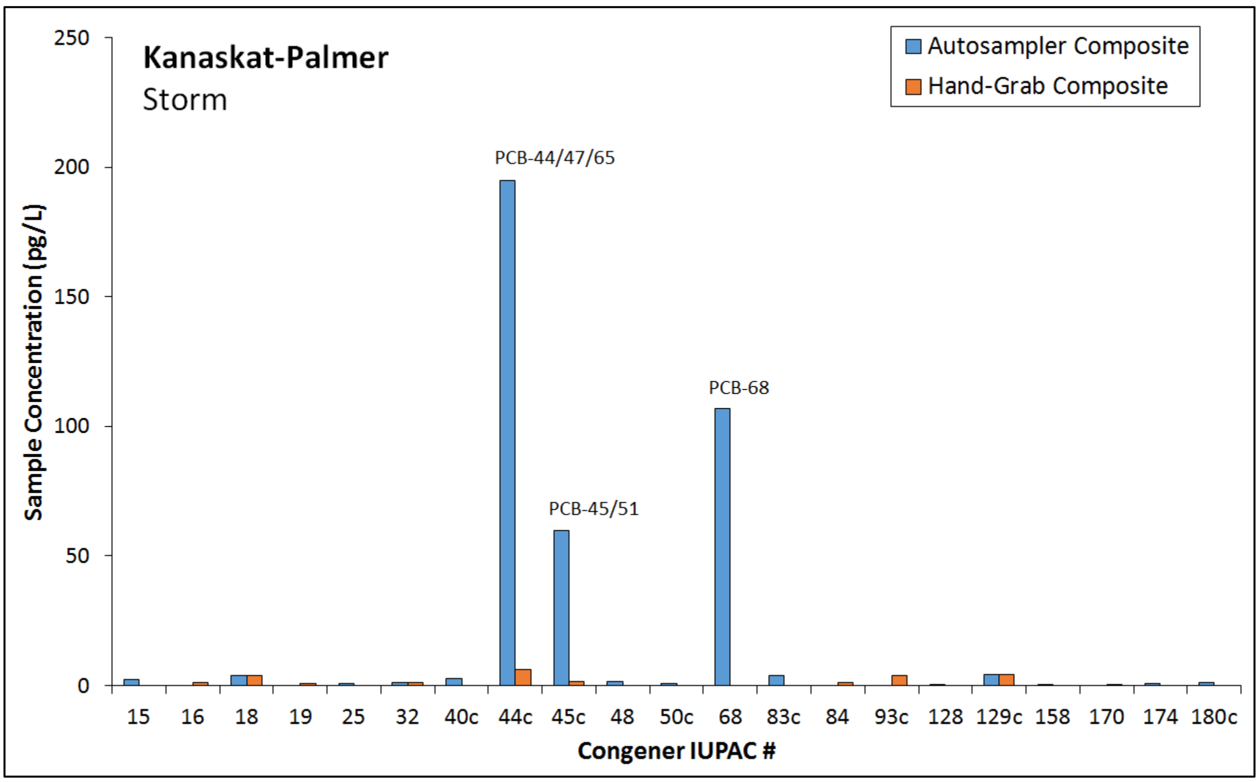


Figure 3. AXYS PCB Congener Concentrations by Sampling Method for Kanaskat-Palmer Storm Event on 4/14/15

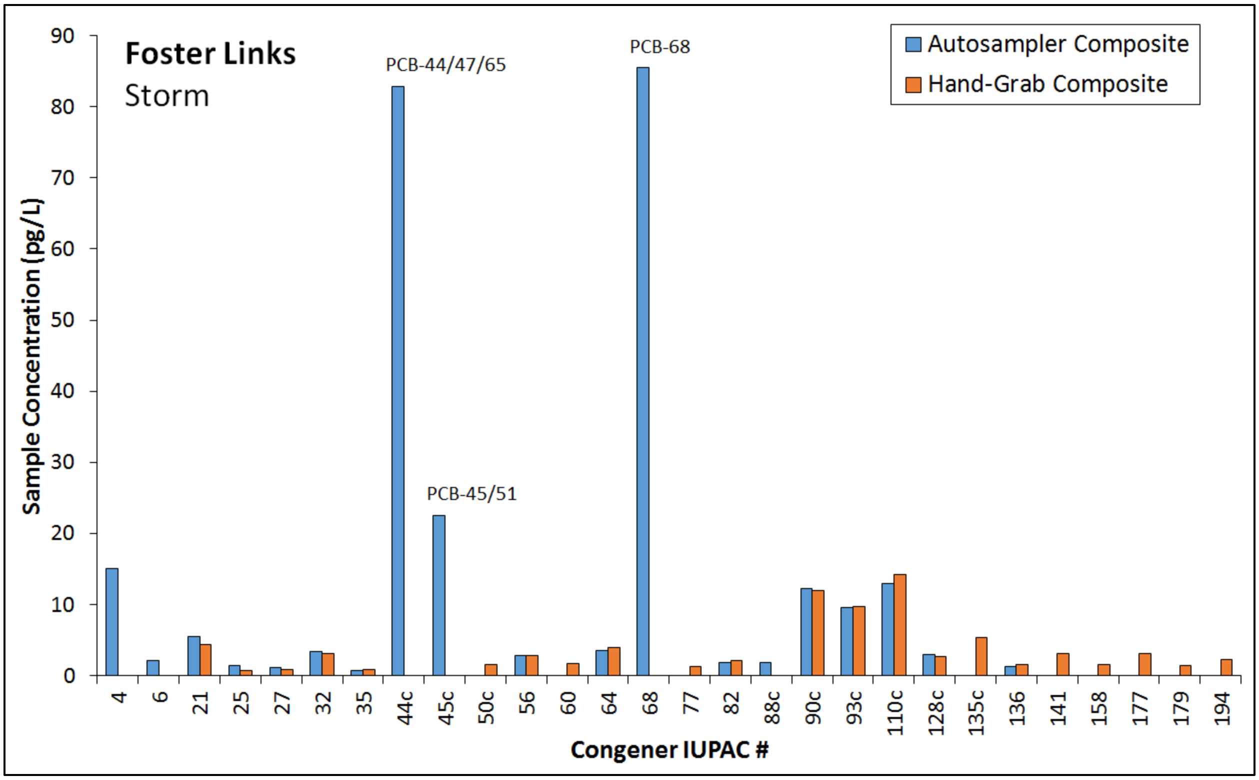


Figure 4. AXYS PCB Congener Concentrations by Sampling Method for Foster Links Storm Event on 12/21/15

Table 12. Contribution of congeners PCB-44/47/48/65, PCB-45/51, and PCB-68 to total PCB concentrations in samples analyzed at both laboratories.

Sample ID	Sample Description	% of Total Contributed from PCB-44/47/48/65[a], PCB-45/51, and PCB-68	
		PRL	AXYS
Autosampler Composite Samples			
L62563-1	Kanaskat-Palmer Storm Event	87%	94%
L64454-1	Foster Links Storm Event	87%	71%
Hand-Grab Composite Samples			
L62563-2	Kanaskat-Palmer Storm Event	0%	32%[b]
L64454-2	Foster Links Storm Event	0%	0%

[a] PCB congeners coelute differently in columns used by each laboratory. Results for congeners PCB-44, PCB-47, PCB-48 and PCB-65 were summed for direct comparisons across laboratories.
[b] Very low concentrations overall - 32% of the total represents 8 pg/L.

4.2 Equipment Blank Sampling Results

Equipment blanks were collected using different tubing types for sample collection and processing, as well as RO water, following methods described in Section 2.2. All silicone tubing was new and pre-cleaned for each sampling event, except for tubing used in the splitting room set-up, as described in Section 2.2. The Teflon tubing was new at the beginning of the project and used for only these equipment blank samples, with decontamination prior to each collection. The PCB results from these samples were used to identify the source of PCB-47, PCB-51, and PCB-68 (Table 13). The following sections describe the findings for each equipment type.

Table 13. Equipment Blank and RO water PCB sample results.

Equipment	Sample ID	Sample Description	Total PCBs (pg/L)	% of Total Contributed from PCB-47/48, PCB-51, and PCB-68
RO water [a]	L63330-4	Splitting Room main sink	13.6 J	19%
	L65645-1	Splitting Room main sink	35.8 J	0%
	L63543-4	Virology Lab main sink	41.9 J	0%
Standard Silicone tubing	L63330-1	8-hour autosampler collection	1,340 J	94%
	L63543-1	7-hour autosampler collection	973 J	98%
	L67549-1	23-hour autosampler collection	132 J	98%
Teflon tubing	L63330-2	Siphoned five times through 20-25-foot Teflon tubing	97.0 J	77%
	L63543-2	Siphoned five times through 20-25-foot Teflon tubing	63.2 J	18%
	L66603-1	Siphoned five times through 20-25-foot Teflon tubing	2.96 J	0%
Splitting room tubing	L63330-3	Pumped through 48-inch Teflon and 6-foot standard silicone tubing	156 J	54%
	L63543-3	Pumped through 48-inch Teflon and 6-foot standard silicone tubing	196 J	73%
Platinum-cured silicone tubing	L63772-1	7-hour autosampler collection	33.7 J	0%
	L63772-2	7-hour autosampler collection	43.0 J	0%
	L64487-1	23-hour autosampler collection	15.3 J	53%

J – estimated sum

[a] RO water serves as control for the equipment blank samples; all equipment blanks tested RO water exposed to each type of tubing.

4.2.1 RO Water

Total PCB concentrations were relatively low in the RO water collected from both laboratory sinks (Table 13); the average total PCB concentration was 30.4 pg/L. To help put this into perspective, the PRL analytical method blank concentrations ranged from 14.9 to 131 pg/L. Contributions from PCB-47/48, PCB-51, and PCB-68 were negligible. The RO water serves as a control for the various equipment blank samples because it was used to create the equipment blank samples. Therefore, when equipment blank sample results are similar to the RO water results, it is unlikely that equipment is a significant source of PCB contamination to the environmental samples.

4.2.2 Standard Silicone Tubing

PCB concentrations in samples collected with standard silicone tubing (Versilic SPX-5) were comprised of over 90% PCB-47/48, PCB-51, and PCB-68. Total PCB concentrations for these samples were one to two orders of magnitude higher than levels in the RO water samples. These data indicate the silicone tubing was a major source of PCBs to the equipment blank samples.

Notably, the silicone tubing equipment blank samples collected over seven and eight hours had substantially higher PCB concentrations than the blank sample collected over 23 hours (roughly 7 and 10 times higher, respectively; Table 13). While roughly the same volume of water passed through the tubing in each sample, the samples collected over the shorter timespans necessitated pumping aliquots of greater volume at more frequent intervals (i.e., 500-mL per hour compared to 850-mL per 30 minutes). Collecting larger aliquots requires longer periods of pumping, which heats and bends the tubing. This physical action of the pump may facilitate release of PCBs into the sample, as suggested by the higher PCB concentrations in blank samples with greater aliquot volumes.

4.2.3 Teflon Tubing

PCB concentrations and congener patterns were quite variable in the Teflon tubing blank samples. Results in the first sample (L63330-2) indicated that Teflon tubing could be a source of PCB-47/48, PCB-51, and PCB-68, while the last sample (L66603-1) did not have detectable levels of these PCB congeners (Table 13). The blank samples were collected through comparable methods and the Teflon tubing was reused each time. The cause of this variability is unknown. It is possible that atmospheric contamination or incomplete decontamination of equipment could have confounded the results.

Total PCB concentrations in two of the three samples collected with Teflon tubing were greater (97.0 and 63.2 pg/L) than the average levels detected in the RO water samples (30.4 pg/L). However, the PCB concentration in the last sample was very low (2.96 pg/L). While concentrations in two of these samples indicate a possible low-level source of PCBs from Teflon tubing, field samples processed with (Section 4.1.2) or collected using Teflon tubing (Section 4.3) do not indicate a concern for PCB contamination. In addition, concentrations of PCB-47/48, PCB-51, and PCB-68 were lower in Teflon tubing blank samples than in the standard silicone tubing blank samples. Based on findings of both laboratory and field samples exposed to Teflon tubing, Teflon tubing is likely a negligible source of PCB equipment contamination.

4.2.4 Splitting Room Tubing

Tubing used for sample splitting includes a combination of previously used Teflon and standard silicone tubing that is decontaminated between each use. Total PCB concentrations were approximately five times higher than levels in RO water samples. PCB-47/48, PCB-51, and PCB-68 represented approximately 54 to 83 percent of the total PCB concentration in the two samples. These findings indicate the current sample splitting process using standard silicone tubing is a likely source of PCBs to environmental samples.

4.2.5 Platinum-cured Silicone Tubing

Total PCB concentrations were relatively low in platinum-cured silicone tubing blank samples (Table 13). The average total PCB concentrations were the same between the tubing (30.7 pg/L) and RO water (30.4 pg/L). PCB-47/48, PCB-51, and PCB-68 were not detected in two of the three samples, and detected at levels similar to RO water in the third sample. These results indicate platinum-cured silicone tubing would not be a source of PCBs to environmental samples, and thus could be used to collect representative autosampler composites for PCBs analysis (as explored in the following section).

4.3 Environmental Samples Collected with Platinum-cured and Standard Silicone Tubing

Total PCB concentrations in environmental samples collected by autosampler with the platinum-cured silicone tubing and Teflon tubing were substantially lower than in those collected by autosampler with the standard silicone tubing and Teflon tubing (Table 14). Conventional parameters were analyzed in both sample types during the first storm event, with very similar results between sampling methods indicating relatively low environmental variability (Table 15).

Table 14. Comparison of total PCB results by autosampler silicone tubing type for each storm event.

Site	Storm Date	Total PCBs (pg/L)		RPD
		Standard Silicone	Platinum-cured Silicone	
Foster Links	05/04/17	756 J	452 J	50%
	05/12/17	488 J	20.6 J	184%

J – estimated sum

Table 15. Comparison of conventional parameter results by autosampler silicone tubing type for each storm event.

Site	Storm Date	Parameter	Parameter Concentration (mg/L)		RPD
			Standard Silicone	Platinum-cured Silicone	
Foster Links	05/04/17	TSS	15.6	14.0	11%
		TOC	2.08	2.05	1%
		DOC	1.80	1.57	14%
	05/12/17	TSS	10.2	NA	NA
		TOC	2.09	NA	NA
		DOC	2.02	NA	NA

NA – not analyzed

As expected, PCB-47/48, PCB-51, and PCB-68 contributed substantially to the total PCB concentrations in samples collected with standard silicone tubing, but contributed negligibly to samples collected with platinum-cured silicone tubing (Table 16; Figure 5). This comparison suggests that platinum-cured silicone tubing and Teflon tubing can be used with autosamplers to collect representative environmental water samples for PCB analysis.

Table 16. Comparison of average contribution of suspect PCB congeners to total PCB concentrations by autosampler silicone tubing type for each site and flow condition.

Site	Storm Date	% of Total Contributed from PCB-47/48, PCB-51, and PCB-68	
		Standard Silicone	Platinum-cured Silicone
Foster Links	05/04/17	27%	0%
	05/12/17	84%	14%

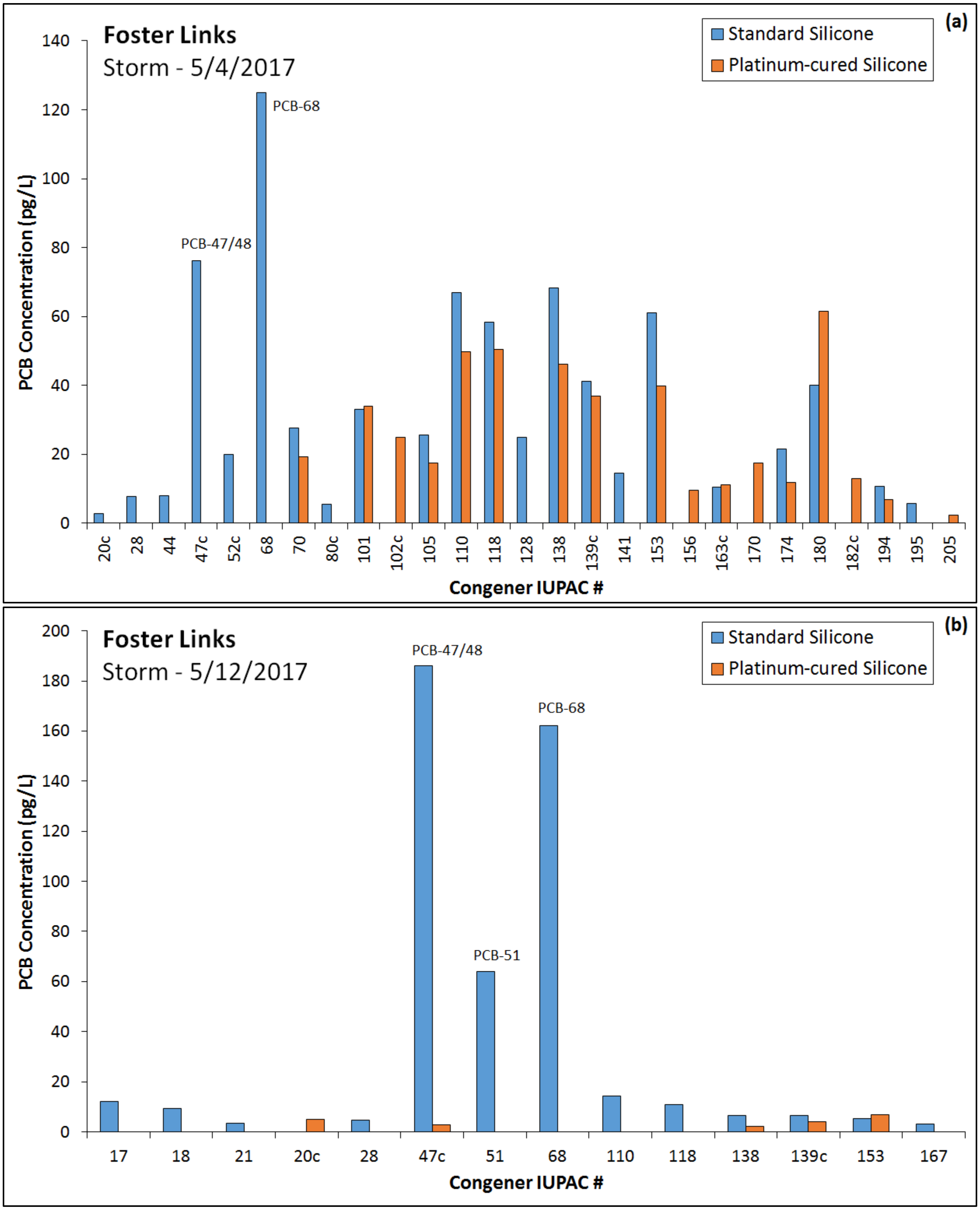


Figure 5. PCB Congener Concentrations by Autosampler Silicone Tubing Type at Foster Links for Storm Events: (a) 5/4/17, (b) 5/12/17

5.0 GREEN RIVER WATERSHED PCB DATA ADJUSTMENTS

From 2013 to 2015, King County collected surface water samples from the Green River watershed for PCB congener analysis using ISCO autosamplers with standard silicone and Teflon tubing, as well as used splitting room tubing for sample processing (King County 2014 and 2015a). Samples were also collected as hand-grab composites from two locations in the Upper Green River Basin, and split into analytical jars at KCEL using splitting room tubing that uses standard silicone tubing (King County 2015a). As detailed in Section 3.0, sampling and splitting methods that use standard silicone tubing can introduce substantial PCB contamination to environmental samples, specifically from PCB congeners PCB-47, PCB-51, and PCB-68. Concentrations of these congeners in Green River samples collected as hand-grab composites without splitting or with platinum-cured silicone tubing had negligible concentrations of these congeners. Therefore, based on the finding of this study, substantial detections of these congeners in previous Green River study samples are not representative of environmental conditions and should be excluded from the total PCB sums and any congener pattern analysis. This only applies to samples collected or processed using standard silicone tubing. Green River samples were collected in previous years that did not include sample exposure to standard silicone or Teflon tubing during sampling or processing.

Unfortunately, due to co-elution of PCB-44/47/65 and PCB-45/51 from the analytical column (SPB Octyl), congeners PCB-47 and PCB-51 could not be quantified in isolation by the laboratory (i.e., AXYS) that analyzed the previously collected samples. However, congeners PCB-44, PCB-65, and PCB-45 do not co-elute with other congeners with the analytical column used by PRL (SGE HT-8 column). Based on the recent PRL data presented in this report, congeners PCB-44, PCB-65, and PCB-45 were rarely detected in Green River samples, and their contribution to total PCB sums was negligible (Figures 1, 2 and 5). Thus, it is reasonable to assume the vast majority of PCB-44/47/65, PCB-45/51, and PCB-68 in samples analyzed by AXYS were contributed by the standard silicone tubing and should be excluded from the total PCB sums for the associated environmental samples. In cases when these PCBs are present in low concentrations in the environment[6], their exclusion from total PCB sums introduces a slightly low bias. However, the adjusted total PCB sums still provide a much more representative estimate of environmental concentrations in these surface water samples.

Below is an overview of how the total PCB concentrations compare with and without the adjustments for PCBs 44/47/65, PCB-45/51, and PCB-68. King County's Green River

[6] PCB-44/47/65 and/or PCB-45/51 were detected in 28 of 42 single grab samples collected from the Green/Duwamish River from 2005 through 2008 (LDW Remedial Investigation database; Windward 2010). In each sample, these detections summed to less than 5% of the total PCB concentrations, with the exception of two samples with particularly low total PCB concentrations (i.e., less than 60 pg/L with PCB-44/47/65 and PCB-45/51 detections summing to only 5 pg/L). Detections of PCB-68 were infrequent and negligible (less than 4 pg/L).

surface water data reports (King County 2014 [revised 2018a] and King County 2015a [revised 2018b]) have been revised to include adjusted PCB totals to better reflect environmental conditions without influence from equipment contamination.

Middle and Lower Green River Watershed (King County 2014)

Figure 6 illustrates the average contribution of PCBs associated with use of the standard silicone tubing (i.e., congeners PCB-44/47/65, PCB-45/51, and PCB-68) to total PCB concentrations for the data originally presented in King County 2014. These congeners were detected at higher concentrations in storm samples than in baseflow samples. Sampling methods for this project required that autosampler tubing be decontaminated with detergent, RO water, and acetone between each baseflow sampling event. However, the acetone rinse was discontinued for storm event samples after observed interferences with TOC/DOC analysis. Reuse of the standard silicone tubing without acetone decontamination may have contributed to greater PCB equipment contamination. Age of tubing could have been an additional factor, because tubing stressed from use may more readily leach contaminants.

Upper and Middle Green River (King County 2015a)

Figure 7 illustrates the average contribution of PCBs associated with use of the standard silicone tubing (i.e., congeners PCB-44/47/65, PCB-45/51, and PCB-68) to total PCB concentrations for the data originally presented in King County 2015a. The congeners associated with standard silicone tubing contributed more to the total PCBs in the Kanaskat-Palmer samples (which came into contact with silicone tubing during collection with autosamplers and the sample splitting room process) than the Upper Green and Sunday Creek samples (which were collected as hand-grab composites that came into contact with silicone tubing only during the sample splitting room process) (Figure 7). In addition, PCB-44/47/65, PCB-45/51, and PCB-68 in baseflow samples at Upper Green and Sunday Creek represented a larger fraction of total PCBs when compared to levels in storm event samples. This difference could be due to the periodic replacement of splitting room tubing.

Overview of Previous PCB Data Collected by King County

Figure 8 illustrates the comparison of total PCB data between grab samples that were never exposed to standard silicone or Teflon tubing and samples collected with standard silicone and Teflon tubing. Before sample result adjustment, PCB concentrations in autosampler-collected storm event samples were quite variable at each site. Following adjustment of the data, results indicate that much of the variability in the Foster Links, Kanaskat-Palmer, and Upper Green data was due to equipment contamination. Less variance was observed in the baseflow data.

Recommendations

Based on the findings of this study, future collection of samples to be analyzed for PCBs should not use standard silicone tubing. Any PCB results for samples collected by autosampler with standard silicone tubing should be reviewed for interferences from

PCB-47, PCB-51, and PCB-68. Decontamination of silicone tubing with acetone may mitigate the severity of contamination, but could cause high bias for organic carbon analysis (Elliott 2013). The study results indicate platinum-cured silicone tubing and Teflon tubing are acceptable forms of tubing for samples collected for PCB analysis.

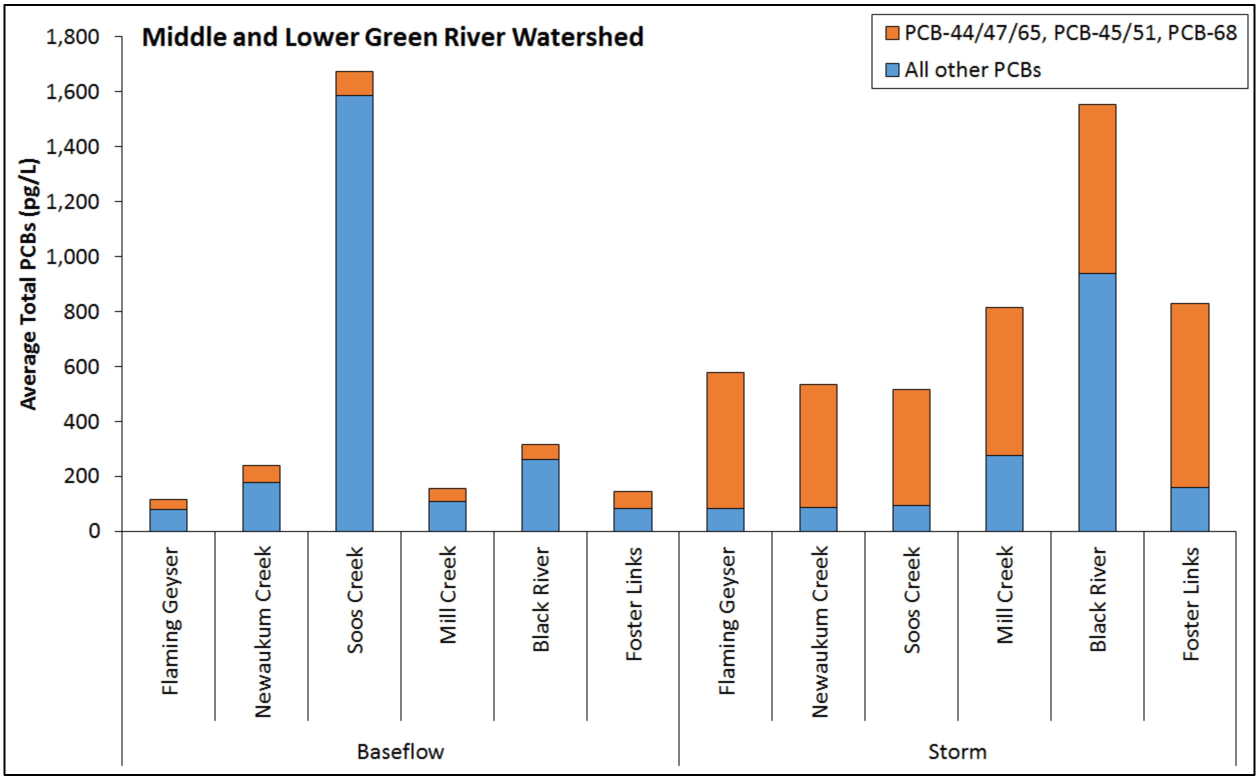


Figure 6. Average composition of total PCB concentrations by flow condition for each Middle and Lower Green River Watershed site (data originally presented in King County 2014).

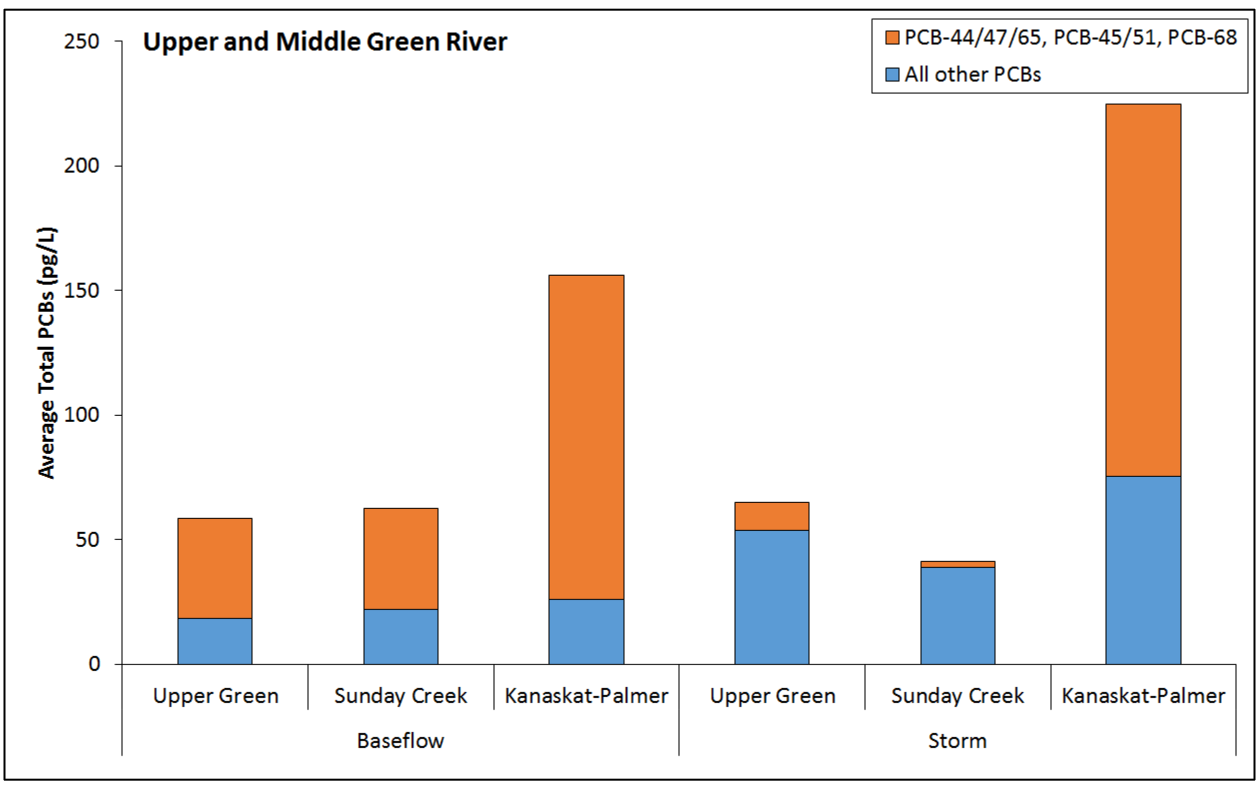
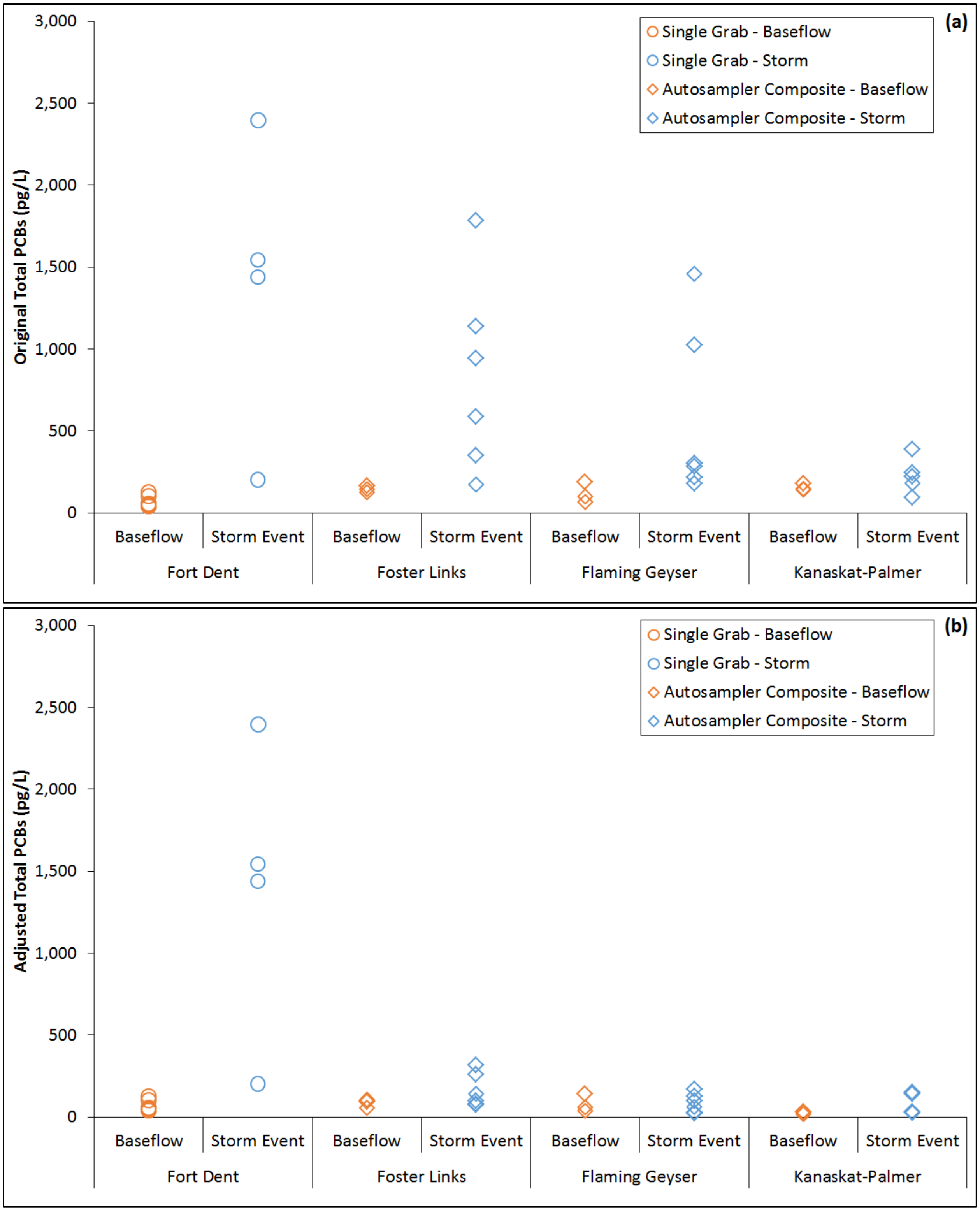


Figure 7. Average composition of total PCB concentrations by flow condition for each Upper and Middle and Green River site (data originally presented in King County 2015a).



Note: the Fort Dent samples were grab samples not exposed to silicone or Teflon tubing.

Figure 8. Historical Green River mainstem data: (a) original PCB totals, (b) adjusted PCB totals.

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