TETRA TECH

Memo

To: EPA Region 10 and Washington Department of Ecology

From: Tetra Tech

Date: June 9, 2015

Subject: Green/Duwamish River Watershed PLA – Data Gaps and Pollutant Groupings (Revised Draft)

The May 2014 report, "Green/Duwamish River Watershed Pollutant Loading Assessment Technical Approach" (Technical Approach) includes a summary of existing environmental data (through approximately 2012) for the Green-Duwamish watershed and the Lower Duwamish Waterway (LDW); and a summary of the existing computer models that have been developed to simulate water, sediment, solids, or pollutants in the watershed.

The Technical Approach proposed use of the following linked modeling tools: the LSPC[1] watershed model, the EFDC[2] receiving water model, and the Arnot and Gobas and DYMBAM[3] food-web models. Use of these models requires a variety of background data, "external forcing" data for model configuration, and supporting data for model calibration and validation. Following development of the Technical Approach, a technical memo summarizing data needed to support the development of a linked watershed / receiving water / food web model (FWM) was developed and entitled, "Existing Data and Model Evaluation" (dated February 2015).

The previous technical memo suggested that hydrology and hydrodynamics data to support LSPC and EFDC development were generally available and not expected to be an obstacle for model development. For water quality, it was suggested that data were available to support LSPC, EFDC, and FWM configuration and calibration to different degrees depending on the parameter. Calibration data are sufficiently available for some parameters, but are limited for others. Recent and ongoing data collection by USGS, Ecology, King County, and the Army Corps of Engineers (ACOE) were deemed critical supplements to the available data, particularly for the watershed model. Finally, development of the linked models are benefitting from the foundation laid by previous modeling efforts.

This "Data Gaps and Pollutant Groupings" technical memo builds upon this previous work with a focus on a more narrow set of parameters that have been identified by Ecology and EPA. First, aspects of pollutant behavior for the prioritized candidate pollutants and recommendations on pollutant grouping are presented. Additional discussion is provided on model development approaches for the selected parameters in the context of the available data. Finally, data and knowledge gaps are summarized along with strategies for addressing these gaps.

The memo is organized into 3 primary sections (excluding the introduction, references, and appendices).

In Section 1, a discussion is provided for pollutant behavior and grouping recommendations for candidate pollutants.

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[1] Loading Simulation Program - C++
[2] Environmental Fluid Dynamics Code
[3] Biodynamic Model of Bioaccumulation

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In Section 2, foundational information from RI/FS and previous LDW modeling is presented along with a discussion of gaps and strategies for EFDC, CSOs, and the food web modeling.

In Section 3, data or knowledge gaps for the watershed are discussed in the context of model construction and source attribution.

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1.0 CANDIDATE POLLUTANTS AND POLLUTANT GROUPINGS

Ecology and EPA have identified a set of pollutants that are candidates for modeling in the Green-Duwamish River Watershed Pollutant Loading Assessment. These candidate parameters constitute a fairly diverse mix of lipophilic chlorinated hydrocarbons (PCBs, dioxins/furans), polyaromatic hydrocarbons (PAHs), one phthalate, and metals (Table 1).

The candidate parameter list is expected to be refined based on this memo and additional discussions. For example, it has not yet been decided how PCBs or cPAHs will be modeled. Total PCBs contain a mixture of up to 209 individual congeners, which can be sorted into 10 homolog groups based on the number (1 to 10) of chlorine atoms attached to the biphenyl ring structure. In addition, there is interest in both dissolved and total metals.

Table 1. Candidate chemicals for modeling (listed in order of priority)

Parameter	Fate and Transport	Food Web	Justification
PCBs	Y	Y	High concern to both WQ and CERCLA, accumulate in biota, fish consumption advisory, recontamination potential
Carcinogenic PAHs (cPAHs; benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h) anthracene, indeno(1,2,3-cd) pyrene)	Y	Y	High concern to both WQ (most 303d listings) and CERCLA, accumulate in biota, ecological concern, recontamination potential
Dioxins/Furans (2,3,7,8 TCDD)	Y	Y	High concern to both WQ (most 303d listings) and CERCLA, accumulate in biota, ecological concern, recontamination potential
Arsenic (inorganic)	Y	N	Concern for both WQ and CERCLA- natural background issue
Phthalates (Bis-2EH phthalate)	Y	Y	Primarily concern for CERCLA, recontamination potential, accumulates in biota- surrogate for other phthalates
Copper	Y	N	Aquatic toxicity concern for ESA species- indicator for built environment
Zinc	Y	N	Aquatic toxicity concern for ESA species- indicator for built environment
Mercury	Y	?	Limited 303d listings, concern for CERCLA, fish consumption advisory

The type and amount of data available for each constituent varies, and data availability will have an important influence on modeling strategy. For example, mercury is of interest, primarily as a contaminant of fish tissue, but the form of mercury that accumulates in tissue is almost entirely methylmercury. There are few sample data for methylmercury, however, so any analyses based only on existing data would need to focus on total mercury as a surrogate for methylmercury.

Ecology's Toxics Cleanup Program under the Model Toxics Control Act (MTCA) adopted a rule amendment[4] for evaluating toxicity and carcinogenic risk for mixtures of dioxins/furans, cPAHs (carcinogenic PAHs), and PCBs when establishing cleanup levels based on a human health risk assessment. The rule requires that mixtures of the compounds in these groups be considered as a single hazardous substance with respect to compliance with cleanup and remediation levels and consider the respective toxicity equivalency factor (TEF; for dioxins/furans and dioxin-like PCBs [Van den Berg et al., 2006]) and potency equivalency factor (PEF) for cPAHs[5]. This rule also requires that cleanup levels consider impacts in a receiving medium based on the TEF concept and that "the congener-specific physical and chemical properties shall be considered during that assessment." While the MTCA is not explicitly a surface water quality program its risk-assessment guidance is likely applicable to surface water quality targets under narrative water quality standards that state[6]: "Toxic substances shall not be introduced above natural background levels in waters of the state which have the potential either singularly or cumulatively to adversely affect characteristic water uses, cause acute or chronic toxicity to the most sensitive biota dependent upon those waters, or adversely affect public health, as determined by the department."

1.1 PCBs

The highest priority constituents for the PLA are the PCBs. PCBs are of concern for both carcinogenic risk and non-carcinogenic toxicity. Human health cancer risk is primarily driven by a small number of dioxin-like PCB congeners. Washington's water quality standards for PCBs are expressed as total PCBs (WAC 173-201A-240); however, a risk-based analysis based on TEFs may also be relevant under narrative water quality standards, as noted above. The modeling may thus need to produce estimates of total PCBs for direct evaluation of attainment of numeric water quality criteria, but may also need to consider the TEF of dioxin-like PCBs in water and fish tissue, while taking into account the physical-chemical properties of individual congeners. However, treating all 209 PCB congeners as independent state variables is not feasible for this modeling project.

Extensive data on PCBs – primarily on PCBs in sediment and associated with solids in and around the LDW – are available as a result of the CERCLA RI/FS process. Approximately half of the available monitoring data on PCBs are resolved to the congener level, while the remainder are quantified as Aroclor[7] equivalents (Aroclors are commercial *mixtures* of various PCB congeners, and the implications and usability of Aroclor-based quantitations are discussed further below).

PCBs are a group of synthetic organic chemicals composed of two phenyl rings with varying numbers of chlorine atoms in various positions (a total of 209 congeners). PCBs are generally oily liquids or solids. PCBs do not break down easily and they can cycle between air, water, and soil, traveling long distances attached to particles. The more chlorine atoms the PCB contains, the more slowly it breaks down. PCBs adsorb (stick) strongly to lipids and organic carbon in soil particles and are not usually carried through the soil by rainwater unless oils or solvents solubilize them.

The behavior of individual PCBs in the environment is largely controlled by the degree to which it partitions between water and sorbents (represented by a partition coefficient that can be defined relative to soils (K_d),

[4] WAC 170-340-708; see Washington Department of Ecology, October 12, 2007. WSR 07-21-065, Order 06-10. http://apps.leg.wa.gov/documents/laws/wsr/2007/21/07-21-065.htm, accessed 5/25/15.
[5] Adopted by Cal EPA in 2005; Cal-EPA's term "Potency Equivalency Factor" is synonymous in concept to "Toxicity Equivalency Factor" and the two terms are used interchangeably here.
[6] WAC 173-201A-240, https://fortress.wa.gov/ecy/publications/documents/0610091.pdf, accessed 5/26/15.
[7] Aroclors were marketed in the United States under the trade name Aroclor by Monsanto (Solutia). Specific Aroclors were developed by varying percentages of individual congeners in a mixture and named for the overall average degree of chlorination of the 12-carbon biphenyl molecules, i.e. a specific Aroclor, Aroclor 1260, has an average chlorination of 60%.

organic carbon (K_{oc}), or the solvent octanol (K_{ow})) and their solubility/volatility (represented by a Henry's Law coefficient (He), defined here as the ratio of the equilibrium partial pressure of a chemical in the gas phase to the aqueous-phase concentration). It has long been known that sorption and desorption of PCBs in the environment is a complex phenomenon including labile and recalcitrant components that operate at different rates and do not always fit assumptions of reversibility (e.g., Carroll et al., 1994); however, many simulation models assume instantaneous and reversible equilibrium sorption. Although a simplification, examination of the environmental behavior of PCBs under steady-state equilibrium assumptions is a useful tool for examining the importance of likely fate and transport pathways. Equilibrium partition coefficients and Henry's law constants together with other fundamental chemical properties can be used to define where chemicals are likely to accumulate in the environment, an approach often referred to as fugacity models. For instance, the Equilibrium Concentration (EQC) model is a screening tool that predicts the distribution of a chemical between soil, water, and air compartments in an idealized "unit world" based on these properties (Hughes et al., 2012), while the Quantitative Water Air Sediment Interaction (QWASI) model uses the same principles to predict the steady-state distribution of an organic chemical within a waterbody given assumptions about loading pathways (Mackay et al., 2014). Models such as this can potentially be used to evaluate the likely distribution of PCB congeners between sediment, water column, and air in the LDW. A similar, but simpler steady-state budget model was earlier developed by Chapra (1991) and provides an easy mode of visualization of the medium in which the largest fraction of the mass of a given contaminant is most likely to be found (some mass can be present in all compartments). Essentially, a mapping on logarithmic space defined by sorption (K_{oc} times organic carbon concentration in the water column) and solubility/volatility (He) determines whether a given chemical will predominantly be found in the sediment, water column, or air. Figure 1 shows a Chapra diagram for a range of lighter to heavier PCB congeners, along with 2,3,7,8-TCDD, at particulate organic carbon concentrations of 0.25 and 5 mg/L using selected literature values for K_{oc} (Environment Agency, 2008) and He (Sander, 2014) . At higher organic carbon concentrations most PCBs and 2,3,7,8-TCDD are firmly in the "sediment zone"; while at low organic carbon concentrations some of the lighter PCBs (mostly mono- and di-chloro congeners) are found in the "air zone", indicating that they will tend to volatilize. None show a preference for the water zone, which is why PCBs are typically present in the water column at only a small fraction of the concentration in sediment.

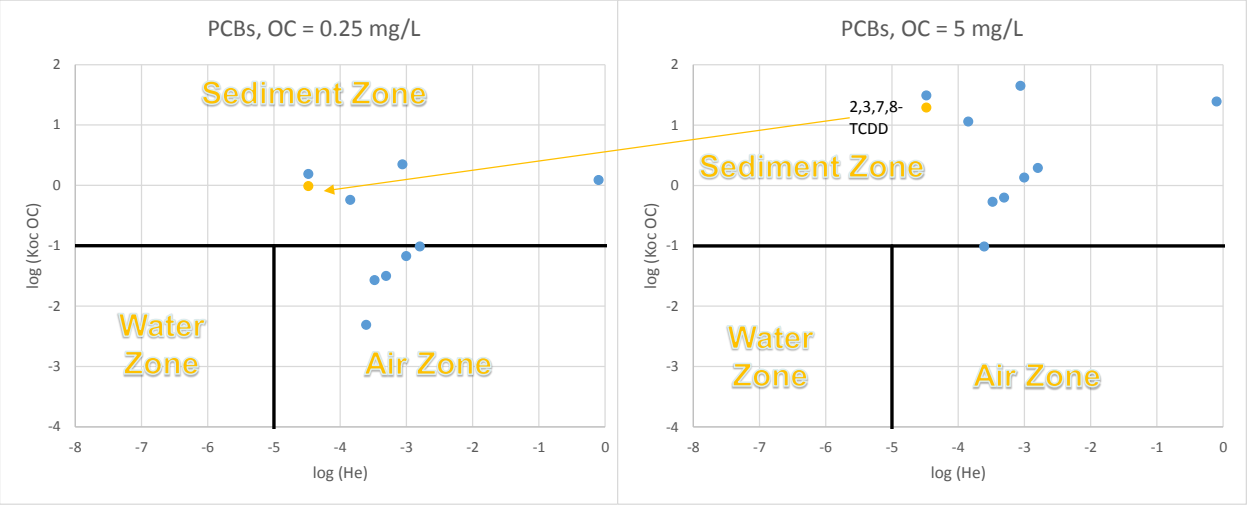

Figure 1. Chapra diagram for distribution of a range of PCBs (blue dots) and 2,3,7,8-TCDD (yellow dot)

Analyses of this sort suggest the feasibility of modeling individual PCB congeners. There are, however, a number of caveats. First, the analysis is based on steady-state assumptions of equilibrium, instantaneous, reversible

partitioning between solid and dissolved phases. In the real world, equilibrium is fleeting and there is ample evidence of slow adjustment between compartments, variation in partitioning based on quality of the local solids or carbon, non-reversible sorption, and sorption to a third phase (dissolved, rather than particulate organic carbon). This results in a situation in which effective partition coefficients at a given site can deviate by an order of magnitude from those reported in the literature or derived from octanol-water partitioning analyses, as was demonstrated in the Hudson River (Butcher et al., 1998). For the LDW and Green River there is a lack of dissolved or pore water PCB analyses with which to estimate site-specific partitioning behavior (which may differ in the water column and sediment due to differences in the quality of sorbent). There is also uncertainty in estimates for He; for instance, the inverse He values reported by Sander (2014) for the dioxin-like congener PCB-126 range from 0.016 to 0.1 mol/(m^3-Pa). Thus, the ability to distinguish behavior of individual congeners in the environment may be somewhat illusory; however, lumping total PCBs together is also not satisfactory, given the wide range of variability in properties. Within the previous Food Web Modeling, ambient PCB data was used to calculate an average concentration weighted K_{ow} for total PCBs in order to examine tissue impacts associated with PCBs. As a result of uncertainties in the K_{ow} (varies over 3-4 order of magnitude for the full congener list), the Food Web Modeling contained large uncertainty in the predicted water column concentration and tissue concentration in future scenarios. Reducing the uncertainty would require modeling that reflects the range of chemical properties of the individual congeners by simulating PCBs as a mixture of congeners or groups of congeners with similar properties.

In sum, simulation of PCBs as a single constituent is not recommended because of the wide range of variability in fundamental properties exhibited by individual PCB congeners. There is a potentially significant data gap for simulation of PCBs in the LDW due to the lack of information on site-specific partitioning behavior. To fully determine appropriate site-specific partition coefficients for PCB congeners or groups, split sample analysis of whole water and filtered PCB concentrations in the water column and bulk sediment and pore water concentrations in the sediment would be needed.

Toxicity is also variable among congeners. The World Health Organization established Toxicity Equivalency Factors (TEFs) for 12 dioxin-like PCBs for human exposures (Table 2) that reflects the their toxicity relative to 2,3,7,8-TCDD. Considering these congeners permits a calculation of the overall toxicity related to the most toxic PCB in water and sediments. The most toxic congeners are PCB-126 and PCB-169. TEQs calculated for the sediments in the RI (Table 4-25 of the RI) for the LDW indicated that PCB-126 (3,3',4,4',5-pentachlorobiphenyl) contributed to over 50% of the Total PCB TEF, followed by other penta- and hexa-homolog members (PCB-105, PCB-118, and PCB 156; PCB-169 was not calculated).

Table 2. Dioxin-like PCB congeners with established TEFs (van den Berg et al., 2006)

Chemical Structure	IUPAC Number	TEF
3,3',4,4'-TeCB	PCB-77	0.0001
3,4,4',5-TeCB	PCB-81	0.0003
2,3,3',4,4'-PeCB	PCB-105	0.00003
2,3,4,4',5-PeCB	PCB-114	0.00003
2,3',4,4',5-PeCB	PCB-118	0.00003
2',3,4,4',5-PeCB	PCB-123	0.00003
3,3',4,4',5-PeCB	PCB-126	0.1

Chemical Structure	IUPAC Number	TEF
2,3,3',4,4',5-HxCB	PCB-156	0.00003
2,3,3',4,4',5'-HxCB	PCB-157	0.00003
2,3',4,4',5,5'-HxCB	PCB-167	0.00003
3,3',4,4',5,5'-HxCB	PCB-169	0.03
2,3,3',4,4',5,5'-HpCB	PCB-189	0.00003

One approach for recognizing the variability of individual congener properties and reducing the complexity of modeling PCBs is to examine homolog groups. The homolog groups (mono- through decachlorobiphenyls) are identified by the number of chlorine atoms attached to the biphenyl structure. For the homolog groups, the boiling point, log K_{ow}, and bioconcentration factors generally increase by 1.6X, 4000X, and 4000X, respectively, per unit increase in the chlorine content. Vapor pressure, solubility in water, and volatilization show a corresponding decrease by 6, 4, and 7 orders of magnitude. The toxicity analysis can generally be based on a ratio to total penta- and hexachlorobiphenyls, as shown above. Further, the high degree of variability and uncertainty in sorption and Henry's law coefficients for a single congener suggests that little precision would be lost by lumping homologs.

It is likely not necessary to model all ten PCB homolog groups. The PCBs in the Delaware River were modeled using a four-homolog model of tetra-PCB, penta-PCB, hexa-PCB, and hepta-PCBs to support a TMDL for PCBs in the estuary (Suk and Fikslin, 2011). Results of the modeling were in general agreement with observed values for water column and sediment total PCBs (primarily more highly chlorinated congeners in this system) based on spatial, bivariate, and cumulative frequency distribution plots. Hindcast simulations indicated a reasonable prediction of water column, sediment, and fish tissue total PCB concentrations, in addition to the homolog groups. Based on the success, the homolog approach should be considered for the Duwamish Waterway and Green River.

The Delaware River approach would not yield an estimate of total PCBs if congeners outside the tetra through heptachlorobiphenyl range are present in significant amounts. For modeling the Hudson River PCBs Superfund site, the HUDTOX model (TAMS, 2000) was calibrated for four different forms of PCBs: total PCBs, Tri+, BZ#4, and BZ#52. The calibration focused on Tri+ PCBs, while total PCBs used K_{OC} and He coefficients estimated as weighted averages across the congeners present, stating "This was a consideration in deciding not to calibrate to total PCB concentrations, but rather to focus the calibration on Tri+…"

Various other TMDLs have worked only with total PCBs. The San Francisco Bay PCBs TMDL (San Francisco RWQCB) is based on total PCBs to reflect EPA recommendations on water quality criteria for both aquatic life and human health and does not directly address TEF-based health risk. The Staff Report goes on to acknowledge some of the problems inherent in this approach: "This is a broad designation of total PCBs that can introduce data comparability issues. However, for the purpose of estimating PCBs loads, sources and reservoirs, the introduced error will likely be small compared to the range of PCBs concentrations found in the Bay… We recommend that ongoing PCBs data collection activities in the Bay analyze for a suite of congeners…"

Notably, the San Francisco Bay effort used only a simple box model of PCB fate and transport that treats the entire Bay as a single box and uses typical rates of sorption and volatilization for all PCB congeners.

The Los Angeles Harbor TMDL for PCBs, PAHs, and other organic constituents (Los Angeles RWQCB, 2011) utilized a complex set of linked fate and transport models, but represented PCBs and PAHs only as totals. Equilibrium partition coefficients for total PCBs and total PAHs in sediment were estimated based on

contemporaneous measurements in surface sediment and overlying water. These partition coefficients were highly uncertain, and "no functional dependence of the partition coefficients on sediment concentration and organic carbon is observed" – possibly because total PCBs and total PAHs constitute mixtures with wide ranges of partitioning behavior for individual constituents.

Thus, both the San Francisco and Los Angeles Harbor TMDLs used simplistic approaches based on total PCBs. This approach was adopted in part due to limited congener data; however, in both cases treating these mixtures as single compounds introduces significant uncertainty into the analysis and is not recommended for the LDW.

Total PCBs is the sum of all measured PCB congeners and represents the entire PCB mass. Tri+ represents the sum of the trichloro- through decachlorobiphenyl homolog groups. This allowed for the comparison of data that was analyzed by congener-specific methods with data analyzed by packed column methods that did not separate the various PCBs as well and did not measure many of the mono- and dichlorobiphenyls. Therefore, use of the operationally defined Tri+ term allowed for a consistent basis for comparison over the entire period for which historical data were available. BZ#4 is a dichloro congener that represents a final product of PCB dechlorination in the sediments. In addition, the physical and chemical properties of BZ#4 are different from the other forms of PCBs (*e.g.,* it is more soluble and has a lower partitioning coefficient), which adds to the rigor of the calibration. BZ#52 is a tetrachlorobiphenyl that was selected as a normalizing parameter for congener patterns based on its presence in Aroclor 1242, the main Aroclor used by General Electric at the Hudson River capacitor plants, and due to its resistance to degradation or dechlorination in the environment. In the LDW, the dominant Aroclors are 1254 and 1260, which are heavier than those that predominate in the Hudson and contain a relatively small fraction of BZ#52. Therefore, another congener would be needed for application of this approach in the LDW.

For surface sediment in the LDW, most PCB analyses are reported as Aroclor equivalents, with less frequent analysis to the congener level from which homologs may be inferred (see below,Table 6). More than half of the congener and Aroclor values are above the detection limit. There are only limited data in the water column of the LDW and Green River (see below, Table 5). Less than half of the congener and Aroclor values are above the detection limit. Use of Aroclor data is somewhat problematic for weathered environmental samples, although still potentially useful. While the original congeners of Aroclor-1260, for example, are present in approximate ratios (or percentages), once released to the environment, shifts may occur in the ratios of congeners present in an environmental sample. While the presence of a high number of samples with values below detection limits represents a limitation, the measurements still provide useful information about where PCBs are known to have low levels.

Each of the specific Aroclors vary considerably in the amounts of specific congeners present in the formulation (Figure 2). Higher Aroclors numbers (Aroclor 1260 vs. Aroclor 1242) are weighted toward more chlorination and higher number congeners while lesser chlorinated Aroclors (Figure 2) tend to contain the lower number congeners. The distribution of specific congeners in parent product (Aroclor 1248 or 1262, for example) is used to estimate specific Aroclors in environmental samples; however, the mixture of congeners in the environment rarely represents a single or mixture of pure Aroclors.

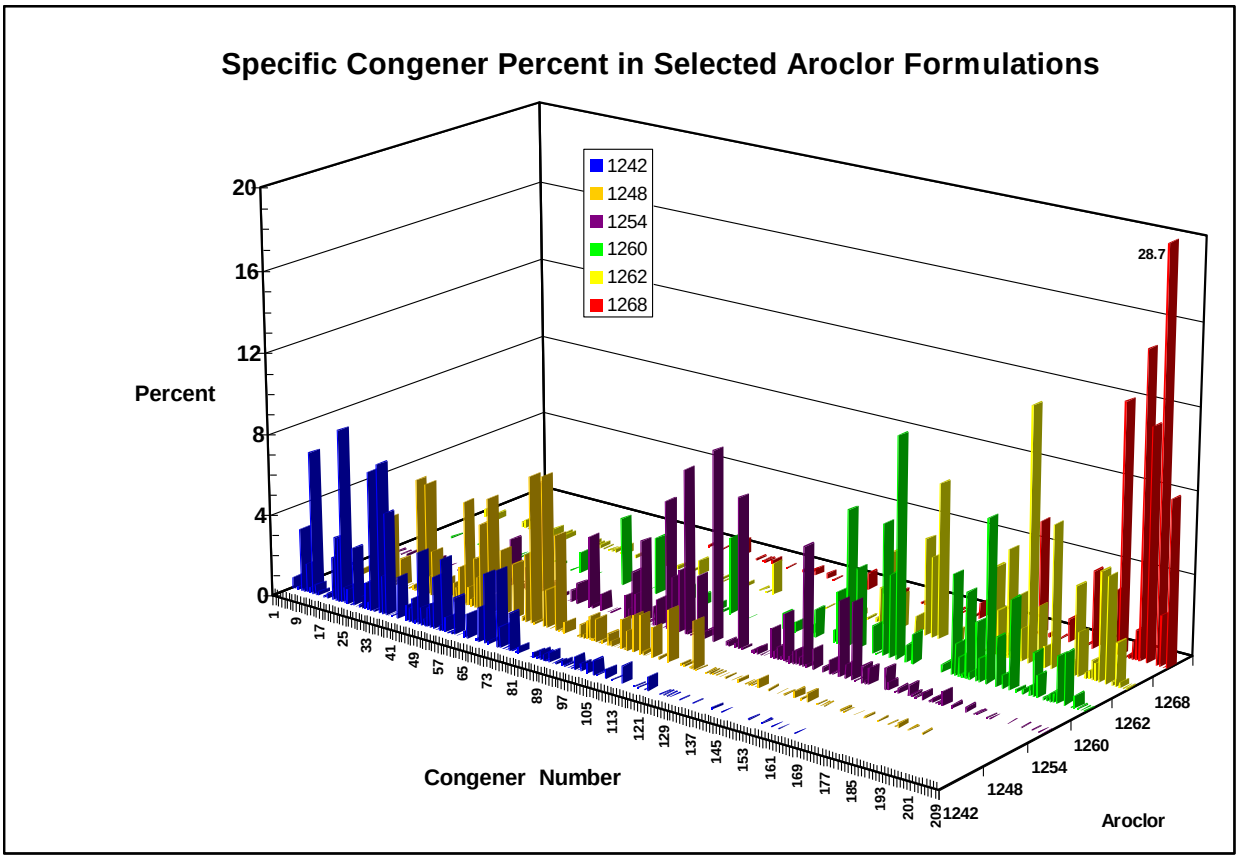

Figure 2. The weight percentage of specific congeners in the various Aroclor formulations (Aroclor 1242 through 1268; Frame et al., 1996)

Using approved analytical methods, analytical chemists base their determination of PCBs in samples as specific Aroclors, i.e., Aroclor-1242 or Aroclor-1260, on comparisons of chromatograms of pure product to chromatograms of the sample. A problem occurs because the process of weathering, including biodegradation and differential solubility and volatility, alters the initial congener pattern of the Aroclor. Also, different lots of the same Aroclor (e.g., 1254) displayed markedly different proportions of congeners (Frame et al. 1996). Therefore, estimating the volume of an Aroclor based on primary chromatogram peaks may misrepresent the actual mass of PCBs. Ecology (2014) has undertaken method comparisons and found that Aroclor measurements generally under-estimate the total mass by PCB congeners (Figure 3).

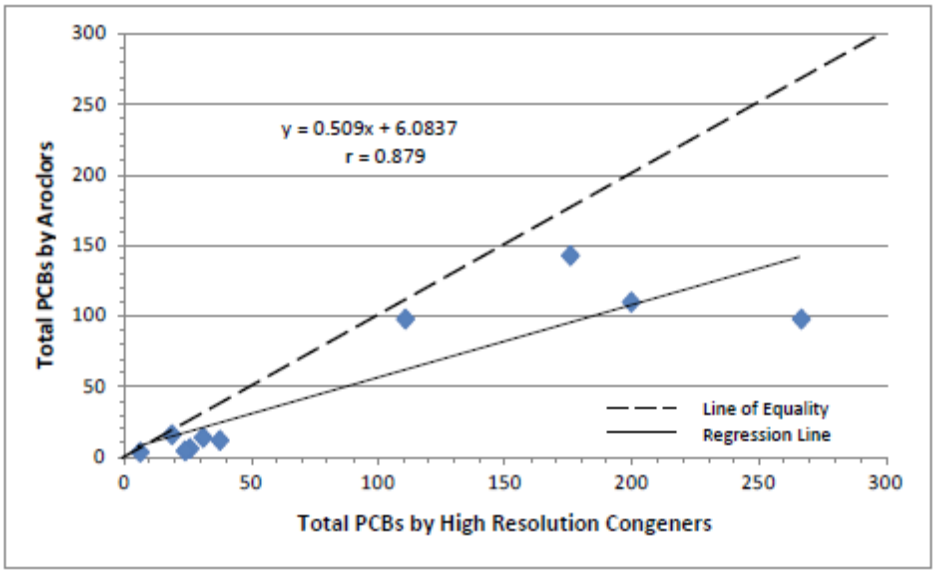

Figure 3. Total PCBs by high resolution congeners and Aroclor analyses

1.2 PAHs

Polycyclic aromatic hydrocarbons (PAHs) consist of two or more benzene rings fused by sharing carbon atoms. They are neutral, non-polar compounds, hydrophobic and considered to be widespread in soil and sediments and are primarily generated by combustion processes. Only a selected set of carcinogenic PAHs (cPAHs) are candidates for modeling in this study. Quantifying only the cPAHs will not provide an estimate of total PAHs, but will provide what is needed for TEQ evaluation of PAH human-health risk. The cPAHs specified (Table 1) are generally those with higher molecular weight.

As with mixtures of PCBs, the individual compounds or those comprising the mixture vary in their physical and chemical properties. In general, for PAHs, increased molecular weight results in decreased solubility in water, increased partitioning and lower volatilization; for example, water solubility decreases by a factor of 10 for each aromatic ring added to the chemical structure. PAHs can be grouped into four useful groups based on properties or toxicity and include 1) carcinogenic PAHs, 2) high molecular weight PAHs (non-carcinogenic), 3) low molecular weight PAHs, and 4) alkalated PAHs. Alkalated PAHs are less understood and characterized in the LDW and much less so in the Green River watershed. The alkalated PAHs are often more persistent than the parent compound, less soluble, bioaccumulate to a greater degree, and show greater adsorption to sediment organic matter.

As with PCBs, PAHs can be characterized in terms of their partition coefficients and Henry's Law constants. A Chapra diagram for a few PAHs (Figure 4) shows that the heavier PAHs are strongly associated with sediment when sufficient organic carbon is present; however, the lightest, 2-ring PAHs are more volatile and tend to be lost to the air. The cPAHs are all in the heavier category.

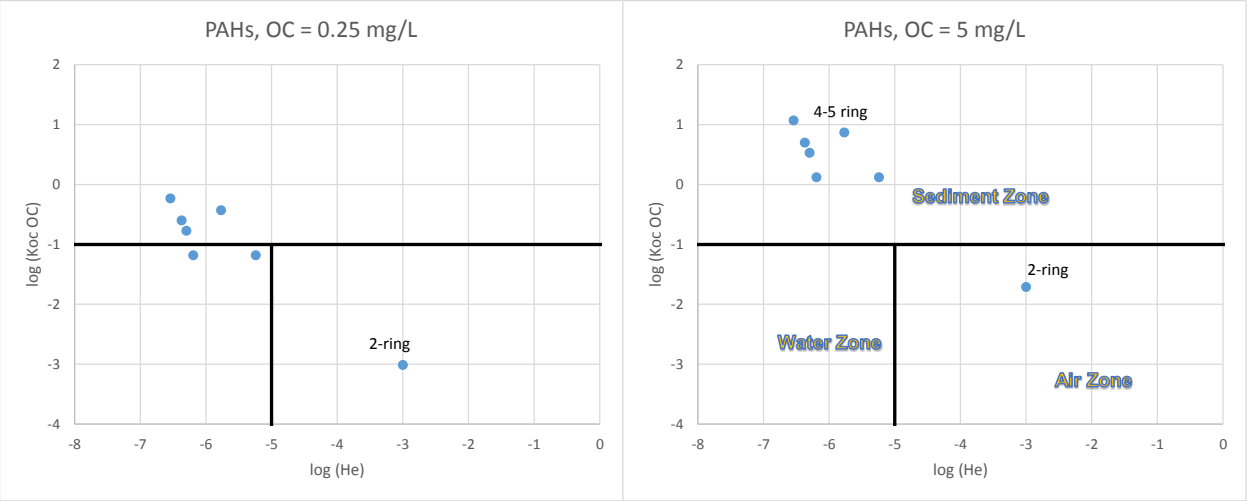

Figure 4. Chapra diagram for PAHs

Effective partition coefficients for PAHs are highly variable which leads to model uncertainty when trying to group dissimilar PAHs for modeling. In one study, the measured partition coefficients of PAHs (naphthalene, phenanthrene, and pyrene) were all different from each other, but individually invariable for different types of "clean soils" or "clean sediment" (Chiou et al., 1998). In another study, it was noted that the K_{oc} for sediments were twice that of soils. Additionally, higher K_{oc} values were observed in coastal sediments contaminated in aromatic-rich wastes due to increased partitioning to sediment organic matter with a greater aromatic ring content. As with PCBs, the variability of the K_{oc} between sediment types and between different PAHs points to a need for a site-specific determination of the K_{OC}s for individual PAHs to support modeling and analysis. Also as for PCBs, lack of paired data on dissolved and sorbed concentrations of PAHs is a data gap at this time.

Industrial urban waterways, such as the Duwamish Waterway, often will contain anthropogenic carbon in addition to naturally-occurring organic carbon, such that use of literature values for predicting partitioning and pore water concentrations will be highly variable (1-2 log units) and overestimate the impacts to benthic organisms (Geiger, 2010). USEPA (2009) suggested that equilibrium partitioning assumptions fail to accurately predict pore-water concentrations of PAHs in systems containing "black carbon" (BC) or "soot carbon" in addition to the naturally occurring carbon because soot carbon more effectively binds the PAHs. It was determined in a study of Boston Harbor (Accardi-Dey and Gschwend, 2002) that black carbon acts in conjunction with natural organic matter (NOM) to determine the overall adsorption of PAHs in sediments and that black carbon may explain the observation of non-linear isotherms for adsorption and bioavailability discrepancies when comparing literature to field studies. Reinterpretation of previous literature datasets showed that a combined black carbon and biogenic/diagenic organic carbon (OC) sorbents can account for sediment-pore water distribution observed in the field and that, to best describe PAH adsorption, three sorbate parameters (K_{oc}, K_{BC}, and n; black carbon distribution coefficient, organic carbon distribution coefficient, and Freundlich exponent) and two sorbent parameters (f_{OC} and f_{BC}; fraction organic carbon and fraction black carbon) were needed (Accardi-Dey and Gschwend, 2003). Black carbon concentrations have also tended to vary in time, with concentrations declining in the Seattle area as higher efficiency standards are implemented for trucks and diesel fuels (e.g., pscleanair, 2013). Characterization of the sorbents within the sediment of the Duwamish Waterway, in particular with respect to black carbon, may be needed to develop a solid modeling framework for individual PAHs in the LDW and is identified as a potential data gap.

In a fully resolved model of cPAHs in the Green-Duwamish system it would be important to apply site-specific knowledge of partitioning and pore-water concentrations to evaluate adverse impacts to aquatic organics and to carry this information forward in the modeling activity (USEPA, 2003). Monitoring data, however, focus on the

total concentration of PAHs in sediment and do not, at this time, provide a sufficient basis for determining site specific partitioning coefficients of cPAHs in the LDW. Without additional site-specific studies on both PAHs and sorbents, it would be most appropriate to model the heavy cPAHs as one group with approximated characteristics. Prior to making this decision, however, analysis should be undertaken to evaluate whether there are significant differences among the ratios of different cPAHs in different locations and media in the watershed.

1.3 DIOXINS/FURANS

Dioxins and furans were suggested for modeling, but initial recommendations from Ecology to the TAC recommended only one dioxin, 2,3,7,8-TCDD, for modeling. This dioxin congener and 1,2,3,7,8-PCDD have the highest TEFs and generally account for the majority of the cancer potency of dioxins/furan mixtures. Therefore, it was suggested that 2,3,7,8-TCDD could serve as a surrogate for total dioxin/furan risk. A moderate amount of data has been collected for dioxins/furans, although not nearly as much as for PCB congeners. The RI/FS database contains 370 dioxin/furan samples, of which 188 are surface sediment grabs and most of the remainder from banks, catch basins, and stormwater solids traps; however, there were no water column samples of dioxins/furans collected for the RI/FS. More recent data collection has included some additional sediment samples along with tissue and water samples and these efforts are ongoing; however, as of April 2015, Ecology's Environmental Information Management (EIM) system contained only 7 surface water and 21 tissue samples for dioxins/furans. There is thus a significant question as to whether currently available data are sufficient to develop a credible model of these constituents.

The physical behavior of 2,3,7,8-TCDD and 1,2,3,7,8-PCDD in the environment is very similar to that of higher molecular weight PCBs (see Figure 1). Given the uncertainties and lack of site-specific data to constrain partition coefficients and Henry's law constants, it may be reasonable to model these dioxins using the same parameter set as specified for tetra- through hepta-PCB homologs. A data evaluation needs to be conducted to evaluate the ratio of 2,3,7,8-TCDD and 1,2,3,7,8-PCDD to one another and to PCB homologs in the tetra through heptachloro range. If the ratios are approximately stable, the PCB homolog groups could be used as a surrogate for dioxin TEFs, with an appropriate multiplier. If not, 2,3,7,8-TCDD and 1,2,3,7,8-PCDD could be represented as one joint or two separate state variables with different source terms, but specified with the same environmental parameters as similar-weight PCBs.

1.4 PHTHALATES

Only one phthalate – bis-2EH-phthalate or DEHP – was identified in Ecology's presentation to the TAC as a candidate for modeling. DEHP has relatively low partition coefficients and Henry's Law constants compared to PCBs and PAHs (using selected literature values for K_{oc} (Environment Agency, 2008) and He (Sander, 2014)) and consistently falls into the Water zone on a Chapra diagram – indicating that the water component of the mass balance is much more important for this pollutant. The different solubility characteristics of DEHP also indicate that it should be modeled as a separate state variable and that none of the other contaminants of concern provides a reasonable surrogate.

1.5 INORGANICS

Priorities four, six, seven, and eight on the list of recommended chemicals for modeling (Table 1) are arsenic, copper, zinc, and mercury. As inorganics, these compounds are present in ionic form, unlike the non-polar PCBs and PAHs, and thus have very different partitioning behavior. Both arsenic and mercury form significant amounts of organic compounds, but it is only in the case of methylmercury that the organic form is a major contributor to toxicity.

A full simulation of all aspects of metal chemistry would require a full ionic balance simulation and consideration of soluble and insoluble complexes – chemistry that is not usually incorporated into the LSPC and EFDC models,

though the MDAS add-on to LSPC addresses metal speciation. Notably, no data on methylmercury concentrations appear to be available. Without additional tools or data to support an alternative approach, the inorganics are likely best approximated in this system in a simplified manner without detailed representation of chemical kinetics in model simulations.

Previous simulation work in the LDW by King County and in Puget Sound has simulated total metals. The dissolved form is most relevant to toxicity. One intermediate level alternative would be to simulate the dissolved fraction based on simplified partition coefficients developed by EPA for the Metals Translator (USEPA, 1996). An approximate partition coefficient to particulate matter (K_P, L/kg) is represented in the following form:

$$K_P = K_{PO} \cdot TSS^{\alpha},$$

where TSS is in mg/L and K_{PO} and α are metals-specific coefficients.

EPA provides a table of default values, but recommends deriving translators based on site-specific data on dissolved and total metals. Sufficient dissolved metals data appear to be available to do site-specific fitting of the metals partitioning and dissolved fraction parameters. It would be a relatively simple matter to modify both EFDC and LSPC to represent partitioning in this fashion and this modification to the code is recommended.

1.6 SUMMARY OF KEY KNOWLEDGE GAPS FOR CANDIDATE POLLUTANTS

As noted above, there are specific knowledge gaps for all of the tentatively selected pollutants. The key knowledge gaps, options to address these gaps, and recommendations for selecting among the options are presented in Table 3.

Table 3. Summary of knowledge gaps and options for candidate pollutants

Knowledge Gap	Options and Recommendations
There is a lack of paired filtered/unfiltered data for site-specific determination of partition coefficients for PCBs, PAHs, dioxin/furans, and phthalates in both the water column and the sediments.	Options: 1. Use literature values that may not reflect local conditions. 2. Collect paired data to evaluate coefficients and improve accuracy Recommendation: Team should consider Option 2.
No data are currently available to directly constrain rates of exchange from the sediment into the water column of non-polar organic pollutants (PCBs, dioxin/furans, PAHs, phthalates), which may be enhanced above typical diffusion rates by biological action.	Options: 1. Treat exchange rates as calibration parameter. 2. Constrain rates based on field evidence. Recommendation: Ongoing work by MIT for USACE may provide field data for the LDW, enabling use of Option 2.
Data for PCBs reported as Aroclors is problematic for comparison to congeners and homologs due to changes in composition from differential weathering. This creates uncertainty in estimating total PCBs as well as the concentration of individual congeners with high TEFs.	Options: 1. Use Aroclor data only, providing a consistent basis for analysis. 2. Assume unaltered Aroclors to interpret congener concentrations and total PCBs from Aroclors; combine with congener data. 3. Use samples analyzed for both Aroclors and congeners to evaluate site-specific relationships between environmentally altered Aroclors and congeners in the LDW. Recommendation: Option 3 is preferable for accurate analysis of PCBs. This takes advantage of available data and allows better specification of kinetic parameters.

Knowledge Gap	Options and Recommendations
Dioxin/furan data are limited, with few water column and biological samples available at this time.	Options: 1. Simulate behavior of selected dioxins/furans using available data and literature coefficients. 2. Delay simulation of dioxins/furans until ongoing data collection efforts produce sufficient information to calibrate a model. Recommendation: Option 2. The same simulation framework employed for PCBs can be used for dioxins/furans once additional monitoring data are available.
For mercury, there is a lack of methylmercury data as well as information on factors that influence methylation (redox, sulfate balance).	Options: 1. Simulate total mercury only. 2. Attempt to simulate mercury methylation using literature values. 3. Collect methylmercury data to support modeling. Recommendation: Option 3 is preferable if mercury is to be modeled; however, lack of data suggests that mercury should not be modeled at this time (see below).
For copper, zinc, and arsenic, the information on competing common ions and chemical conditions appears insufficient for a full analysis of solid and aqueous speciation incomplete to support redox chemistry.	Options: 1. Simulate ionic metals as general quality constituents that can deposit to or erode from the sediment but are otherwise conservative. 2. Represent ionic metals partitioning to solids and solubility using the method recommended by USEPA (1996); modify EFDC and LSPC model codes to represent this behavior. 3. Collect additional data and develop a detailed geochemical simulation. Recommendation: Option 2 appears to be the most feasible alternative for copper and zinc. Option 1 should be sufficient for arsenic.

The knowledge gaps summarized in Table 3 together with the discussions presented earlier in this section in turn have implications regarding the specific constituents that can or should be simulated in the model. The candidate chemicals from Table 1 are revisited in Table 4.

Table 4. Recommendations on chemicals and groupings for modeling

Parameter	Issues	Recommendation
PCBs	Group of 209 congeners with a wide range of chemical properties. Simulating total PCBs as a single state variable will lead to inaccuracies, but it is not feasible to simulate 209 congeners individually.	Simulate a reduced set of PCB homolog groups (fate and transport and food web models).
Carcinogenic PAHs	Group of 8 chemicals with differing properties.	The cPAHs can likely be simulated as a group with approximated characteristics; however, further data analysis is necessary to make a final decision (fate and transport and food web models).
Dioxins/Furans	Data are limited; simulating only 2,3,7,8-TCDD will not represent full toxic potential associated with this group.	Delay modeling until additional data are collected. (Model structure for PCBs will also work for dioxins/furans.)

Parameter	Issues	Recommendation
Arsenic (inorganic)	Determination of natural background concentrations may be an issue.	Simulate inorganic arsenic only using a simplified mass balance approach (fate and transport only)
Phthalates	DEHP was suggested as a surrogate for other phthalates.	Simulate DEHP. Use as a surrogate appears reasonable (fate and transport and food web models)
Copper	Aquatic toxicity evaluation requires dissolved concentration.	Simulate dissolved and sorbed inorganic forms using USEPA (1996) methods adjusted to local data (fate and transport only).
Zinc	Aquatic toxicity evaluation requires dissolved concentration.	Simulate dissolved and sorbed inorganic forms using USEPA (1996) methods adjusted to local data (fate and transport only).
Mercury	Lack of data for methylmercury hampers evaluation of risk and bioconcentration potential.	Do not model mercury at this time.

2.0 LOWER DUWAMISH WATERWAY

An informational basis for the current model planning effort is supplied in the extensive reports, data collection, data analysis, and modeling work undertaken as part of the Superfund investigation of the LDW. A summary of this effort and conclusions that can be drawn are provided, forming a foundation for analysis of data and knowledge gaps relevant to the PLA.

2.1 RI AND FS SUMMARY

The Remedial Investigation or RI (Windward, LLC, 2010) reports on data collected through October 2006 and available as of 2008. Among other things it contains an extensive review of the nature and extent of contamination (Section 4), an evaluation of sediment dynamics and development of a sediment transport model (Section 3), a discussion of "background" concentrations present outside the LDW (Section 7), and an analysis of potential pathways and sources (Section 9). A FWM is documented in an Appendix. The focus of the RI is to a large extent on sediment because the parameters addressed have low solubility and a high affinity for sediment; thus, stores and movement are largely controlled by sediment dynamics. Additional investigations are reported in the Feasibility Study or FS (AECOM, 2012), which also reports on the modeling. The FS supplements the RI dataset by adding samples collected through April 2010 – primarily 174 surface sediment and 509 subsurface sediment samples, along with 2006-2007 tissue data

The RI addresses multiple chemicals of concern (COCs). The ecological risk assessment identified PCBs, cadmium, chromium, copper, lead, mercury, and vanadium as COCs and identified 41 COCs that were toxic to benthic invertebrates based on exceedance of the Washington State SMS SQS values. The human health risk assessment identified 19 COCs, but concluded that the major risk drivers were PCBs, arsenic, cPAHs, and dioxins/furans. The report focuses on these major risk drivers.

The RI provides a comprehensive analysis of the distribution of these COCs, especially in sediment and fish tissue within the LDW, as of 2007. It also presents surface sediment data from areas outside of the LDW including Green River data upstream of the LDW and sediment data from urban bays and lakes, subsurface

sediment data from the Upper Turning Basin, suspended solids data from upstream of the LDW, and data from a variety of pathways and sources studies. Some important conclusions from the RI relative to are:

- The primary risk drivers are associated with legacy releases of chemicals into the environment from a diverse array of individual sources, resulting in large storages of COCs in the sediment of the LDW. The presence of many different sources results in a high degree of heterogeneity in sediment concentrations.
- While extensive work has enabled a good characterization of the distribution of COCs in the sediment as of 2007 it is also clear that the distribution of both sediment stores and upland sources changes over time, due both to environmental processes and ongoing remediation and cleanup activities. The shifting temporal character of the system will present challenges to modeling. Differences between 2007 and current conditions will be especially important to consider.
- Water column data (both total and sediment-sorbed) are relatively sparse and the COCs have low solubility and are mostly associated with sediment. This will pose challenges for calibrating a water quality fate and transport model.
- Residual sources within the storm sewer and combined sewer drainage are extremely heterogeneous and only incompletely characterized (as of 2007), creating a significant challenge for modeling chemical loads. A more feasible goal for watershed modeling may be to characterize flow and solids movement from source areas that can then be associated with site-specific information on COC concentrations, when available.

The most extensive data exist for sediment, with a significant amount of tissue samples as well. In contrast, surface water data available to the RI were limited, consisting of three sampling events conducted for the King County water quality assessment in 1996 and 1997 and during an additional sampling event in 2005. Because the primary risk drivers are high molecular weight, low solubility organic compounds, concentrations in sediment and tissue are expected to be much higher than in the water column, leading to this focus on sediment and tissue samples. However, a surface water quality modeling effort will need more information on water column concentrations, which has been remedied to some extent in sampling since the RI. Other, more specialized sampling campaigns addressed pore water and seep water concentrations for many COCs – although the pore water samples were not analyzed for PCBs, resulting in a gap in data for estimating site-specific partition coefficients.

PCB data are discussed in detail in Section 4.2.3 of the RI. The greatest focus is on surface sediment concentrations, and spatial interpolation methods were used to estimate a complete map of total PCB distribution in the LDW, as well as changes over time at resampled locations. Sample analyses are about evenly split between full congener determinations and analysis as Aroclor equivalents. The RI discusses the comparability of these measures, and further information is available in an Ecology (2014) study. The limited surface water data confirm low concentrations of total PCBs, ranging from 0.1 to about 3 ng/L.

Section 4.2.4 of the RI summarizes arsenic data. As with PCBs, arsenic is well characterized in the sediment and tissue; in contrast to PCBs, dissolved and total arsenic were hundreds of water samples collected in 1996-1997.

PAHs (4.2.5) and BEHP (4.2.6) are also well characterized in LDW sediment and tissue (but not pore water), and had only limited data for surface water concentrations, with low rates of detection in those surface water samples that are available. For both COCs there are over 800 samples meeting DQOs in surface sediment. In contrast, only 54 sediment samples and no surface water samples were available for dioxins/furans at the time of the RI (4.2.7).

Metals are discussed as a group in Section 4.2.6 of the RI. There is not a particular focus on mercury (which has been proposed for the surface water modeling), but mercury was detected in 746 out of 868 sediment samples and maps of the distribution of all metals in surface sediment are provided. The tissue analyses for mercury also appear to provide decent coverage. Only a small number of surface water samples had been analyzed for mercury. One important gap is that it does not appear that analyses were available for methylated mercury, which is the bioaccumulatable form.

The Upper Turning Basin is frequently dredged and sediment quality there is based on core data collected by USACE for dredged material characterization. This is an area in which much of the coarser sediment load from the Green River settles out and must be frequently dredged, so these cores likely provide an integrative measure of upstream sources over time.

Data on both sediments or solids from RM 5 to RM 7 were compiled for total PCBs, arsenic, cPAHs, and dioxins/furans to assess the quality of sediment potentially being transported into the LDW. There were on the order of 55 bedded sediment and 20 or so suspended solids samples for most of these constituents, except that there were only 4 bedded sediment and no suspended solids samples for dioxins/furans. An Ecology bedded sediment study from RM 4.9 to RM 6.5 is noted, but was not received in time for inclusion in the RI. The section does discuss 21 King County unfiltered water samples collected from the Green River at Fort Dent and in 2005 and 2007/8, along with Duwamish River at E. Marginal Way S. in 2007/8, and analyzed for PCB congeners. Arsenic data are available for these dates as well as from 2001-2003 samples (2001-2003 analyses for Aroclors at the same location had detection limits too high to be useful). The 2007/8 analyses included unfiltered cPAHs as well. Total PCB concentrations at Fort Dent varied from 0.04 ng/L to 2.4 ng/L while cPAHs varied from 0.05 to 3.4 ng/L, with higher concentrations during storm events.

The discussion of contaminant concentrations associated with upstream solids is in Section 5.2.3.1 and Appendix C, Part 3 of the FS. An issue worth noting is that the FS focuses almost exclusively on contaminant concentrations in sediment, whereas the upstream King County data are whole water samples. These data "were normalized to the value of the concurrently collected TSS", equivalent to an assumption that 100 percent of the contaminant mass is present in sorbed form, which is a reasonable and conservative approximation relative to recontamination potential of LDW sediments. The FS also uses USACE core data from the Upper Turning Basin as an indicator of the concentrations of PCBs and cPAHs on upstream inputs of suspended sediment. This approach might under-estimate upstream inputs, as it is likely that the concentrations of hydrophobic contaminants are higher on fine and organic solids, whereas deposition in the Turning Basin is preferentially shifted toward the coarser sediment fraction. Normalization of observed concentrations on sediment to organic carbon content may be preferable as a means of estimating the upstream sediment-bound load.

Section 7.3 of the RI summarizes urban background sediment data "for context," and focuses on surface sediment data from various urban bays and lakes outside the LDW. This is potentially useful for establishing general rates of urban loading in the watershed model.

Section 9 of the RI summarizes potential ongoing sources that could lead to sediment recontamination following cleanup of the LDW. These are identified as atmospheric deposition, upstream surface water inputs from the Green River, direct discharges to the LDW including CSOs and storm drains, ground water, bank erosion, and waterway activities in the LDW. Each of these potential source categories is analyzed in detail, providing important information on the state of knowledge and data as of 2007.

Atmospheric deposition (RI 9.4.2) is characterized based on a number of studies, most notably the two phases of King County data collection. Additional data are available since the RI, and these fluxes should be relatively well constrained. In contrast, upstream surface water inputs from the Green River (9.4.3) are relatively poorly constrained, but are not believed to be a significant recontamination risk.

Direct discharges to the LDW (RI 9.4.4 and FS 2.3.3.2) include both CSOs (with emergency overflows) and both public and private separate storm sewer discharges (the latter are about 24% and 15% of the drainage area, respectively, according to FS). It is noted that annual stormwater discharge volume are usually substantially higher than CSO volumes (estimated at 4,000 MG/yr for stormwater versus 75 MG/yr for CSOs). There are some 1990s whole-water samples from two CSOs, but PCBs were not detected, likely due to detection limits. A more extensive body of data is available from sampling of accumulated solids in 245 storm water catch basins from 2002 – 2007. These show the presence of COCs and their concentration in solids, but do not directly measure loading rates. The STM estimated lateral loads to the LDW from storm drains by combining HSPF unit-area simulations of flow with average TSS concentration by land use estimated from 24 locations in Seattle, Bellevue,

Tacoma, Issaquah, and Everett. These lateral load estimates were subsequently updated for the FS and described in Appendix C, Part 4, Scenario 2. The TSS load estimates allow estimation of COC loading.

Groundwater concentration data are available for a number of studies (RI section 9.4.6) and vary significantly by facility. The heterogeneous nature of these concentrations will be challenging to incorporate into a watershed model. It will also be important to assure that the water balance division between surface and subsurface flows is accurately represented. The FS notes that the potential for groundwater transport of COCs will be further assessed as part of Ecology's ongoing remedial investigations.

Two additional significant sources are identified within the LDW. One is bank erosion of contaminated soils and sediments, which appears to be significant despite extensive armoring of the bank. Characterization of erodible material is required at sites where bank construction or remediation is planned. High concentrations are present at some of these sites, but they are also highly heterogeneous so it will be difficult to establish a full characterization for modeling. Finally, routine waterway activities including dredging, in-water structure maintenance, and propeller wash all contribute to resuspension of material stored in the bed of the LDW.

The multiple sources and the highly variable levels of contamination, will present a challenge for watershed modeling. Further information on these issues is being developed as part of Ecology's source control strategy for the LDW. In this process, Ecology identifies priority areas through a tiered process and develops "summary of existing information and data gaps reports." Ecology had developed and published data gaps reports and Source Control Action Plans (SCAPs) for the 24 priority areas adjacent to the LDW. While this type of information is of high value, the number and complexity of sites will make it challenging to incorporate into a watershed-scale model.

The modeling described in the RI/FS consists of a hydrodynamic/sediment transport model (STM; QEA, 2008) and a FWM. The STM is used to predict changes in sediment concentration by combining it with estimates of contaminant concentrations that enter the LDW from upstream and from lateral flows. The LDW was determined to be net depositional and risk pathways are assumed to be controlled by sediment concentrations.

The predicted contaminant concentration in the sediments is estimated via an accounting tool referred to as the Bed Composition Model (BCM; FS 5.2) that combines EFDC estimates of sediment flux and deposition with assumptions about contaminant concentrations on incoming sediment. The BCM assumes that all contaminants are strongly bound to sediment particles and that there are no mass losses due to degradation or volatilization, nor any transfer from suspended sediments to the water column (note that a constant flux velocity of pollutants from sediment to water column is included in the FWM).

The FS cites sources of uncertainty in the model predictions of changes in surface sediment concentration rate of net sedimentation/burial of incoming sediments (5.5.1 and 5.5.2) and the contaminant concentration on those incoming sediments (5.5.3). Section 5.7 of the FS also discusses the role of loss processes, which processes "have not been modeled in the FS," including microbial degradation, volatilization, and desorption. A water quality model could include sediment/water exchange and volatilization losses. In addition, microbial degradation of PCBs may be an important process for water column concentrations. The degradation process tends to produce lower molecular weight homologs that have greater solubility and smaller partition coefficients and are thus more readily exchanged into the water column.

2.1.1 Additional Information from Previous LDW Modeling

The FWM of PCB bioaccumulation that was developed for the LDW Superfund Remedial Investigation required estimates of water column concentrations in the LDW. This was done using an update of the 1999 King County EFDC model of the LDW and is reported in a memorandum from Bruce Nairn to Jeff Stern and Debra Williston dated November 30, 2009 and reproduced as Attachment A to Appendix D (Food Web Model) of the RI report. This earlier application provides some insights into technical issues and data gaps relative to the proposed modeling effort.

The 2009 EFDC modeling addressed total PCBs (as sum of congeners), as requested for the FWM. The effort encountered a number of issues that we have already identified. The calibration objective "was to obtain total PCB predictions that would be within a factor of two when averaged LDW-wide on monthly timescale." Specifically, the calibration was to the 2005 King County sampling, consisting of only four events and two locations.

A key issue was the estimation of partition coefficients for PCBs. A surrogate total PCB partition coefficient was based on octanol-water partition coefficients reported in the literature for PCB congeners, weighted by the observed distribution of congeners (separately for sediment and water column), and converted first to a carbon partitioning coefficient (Koc) and thence to a solids partitioning coefficient (Kd). There were no site-specific data (e.g., paired analyses of filtered and unfiltered samples) to validate the partitioning estimates.

Transfer from the sediment was represented by a flux velocity (rather than a diffusion parameter), for which no direct evidence was available. This was the major calibration parameter in the model (set to 1.0e-6 m/s), but is also an important source of uncertainty. Actual flux is likely to be largely driven by biological activity and should vary seasonally. As implemented "This flux rate is constant in time, and the model does not include any simulation of biological activity or time varying estimates of the sediment flux rate."

Another issue for the 2009 model was the changing conditions in sediment in the LDW. Specifically, sediment remediation in the vicinity of the Diagonal/Duwamish CSO/storm drain occurred in 2004-2005, shortly before the water column data used in calibration was collected, but after the sediment characterization sample collection. This required an effort to estimate the post-remediation sediment concentrations in the area.

The 1999 King County EFDC model simulated (among other pollutants) PAHs, DEHP, copper, and mercury. The model appeared to perform well for copper, but data were not sufficient to quantitatively evaluate performance for the other pollutants of interest to us.

2.2 LOWER DUWAMISH WATERWAY - EFDC

Previous efforts conducted by King County and by consultants for the RI/FS have provided a strong foundation for hydraulic and sediment transport modeling in the LDW using EFDC. In contrast, modeling of the fate and transport of toxics in the LDW is less developed. The Superfund RI/FS work simulated flow and sediment with EFDC, but evaluated toxics only via a mass-balance accounting designed to evaluate how ongoing sources and remediation would affect the concentrations in surface sediment. The original King Co. (1999) EFDC model was set up for several COCs for this project, but, of these, performance could be evaluated only for copper based on the data available at the time. The 2008 update to the EFDC modeling in support of the FWM simulated PCBs, but in a simplified manner (as total PCBs) and with significantly less data than are now, or will soon be available. A major component of work to support the PLA will be building on the existing work to develop a full EFDC simulation of the movement and storages of all the project COCs within both the sediment and the water column of the LDW.

2.2.1 Updated EFDC Model Domain

The model domain for EFDC is an important factor to determine before discussing data needs and gaps for model configuration and calibration. The location of model boundaries may influence data that could be used as boundary conditions for configuration, or data that could be used to support calibration if the boundaries extend.

The EFDC model domain was discussed at the TAC meeting on March 19, 2015. USGS provided information that the tidal influence could reach river mile 17 near Kent, WA under low flow conditions (also discussed in USGS, 2013).Given this factor, there may be cause to extend the upstream extent beyond those used for previous efforts Figure 5 identifies river mile 17 relative to the model domains of the original King County EFDC model and the EFDC model sponsored by the Lower Duwamish Waterway Group (LDWG) for the RI/FS. Both of the prior models stop well short of river mile 17. While it is likely that there is little upstream advective transport at

this point, the tidal influence will affect the hydrodynamics, particularly at a subdaily scale. It may thus be advisable to extend the EFDC modeling up to this point.

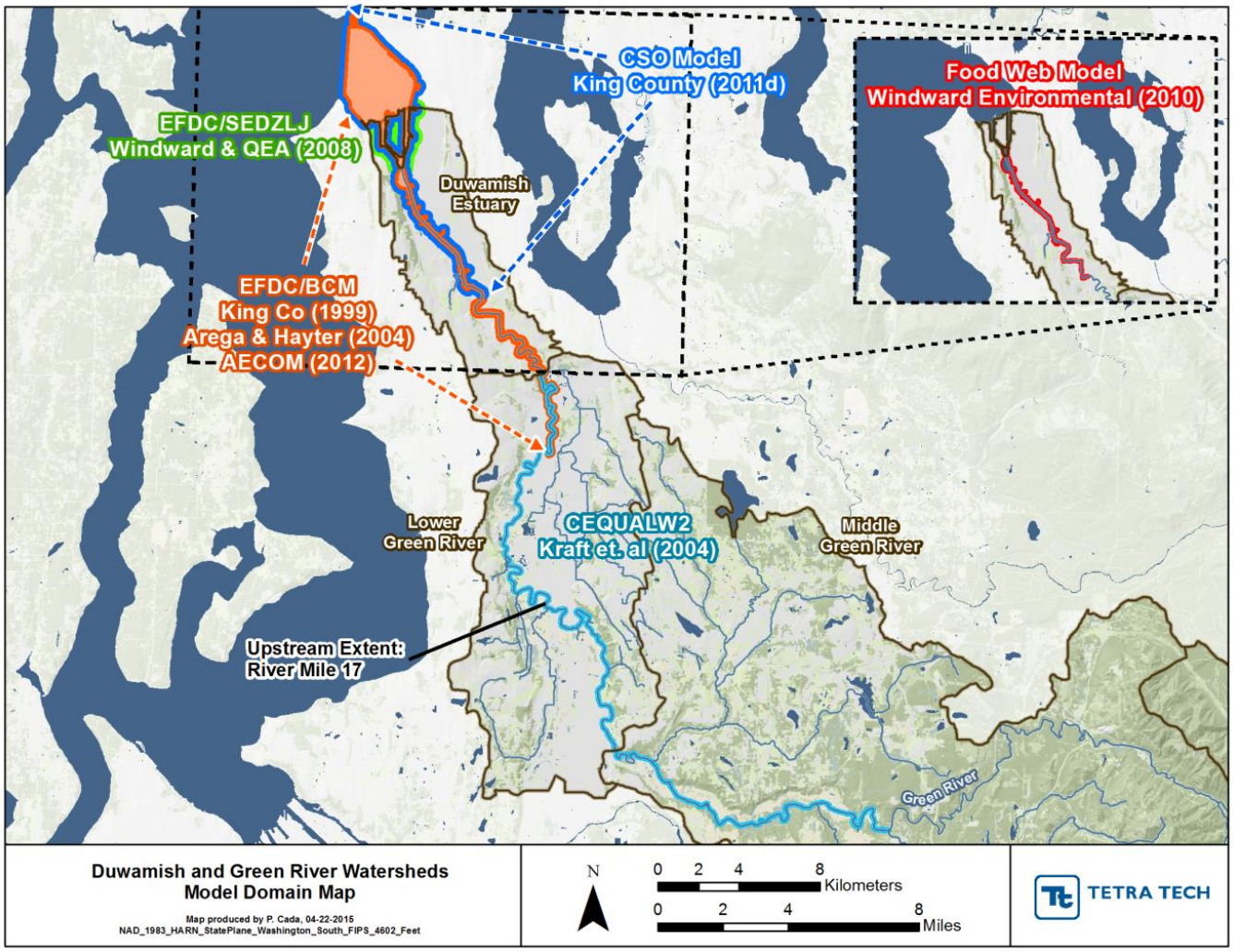

Figure 5. EFDC model domain

If a change to the upstream extent of the model (to river mile 17) were made, the domain would extend upstream approximately 8 miles into the Green River from the confluence of Black River and Green River. Such a change would also influence the watershed model delineation as the location of the EFDC model upstream extent should be a pour point of a sub-watershed in the watershed model so that flow, suspended sediment, and toxics from the watershed model can be readily linked to the receiving water model. With such a change, data in the 8 mile portion of the Green River below Kent, WA could be used to provide the EFDC model background information and to support the EFDC model calibration.

2.2.2 LDW Current Conditions and Additional Data Summary

EPA and Ecology have identified a candidate list of eight chemicals or groups of chemicals for modeling (see Table 1). The eight chemicals or chemical groups are PCBs, cPAHs, dioxins/furans (e.g., 2,3,7,8 TCDD), arsenic, phthalates (e.g., DEHP), copper, zinc, and mercury. Before discussing the strategies of filling the data gaps for model development, the data coverage of these toxics in the LDW was reviewed based on the RI and FS studies and subsequent data collection. It should be noted that the RI and FS focused on the LDW while the proposed

sediment and toxic fate and transport models cover a much larger area than the LDW. Data assembled for the RI/FS process in the LDW have and continue to be augmented by additional data collection in the upstream watershed.

A total PCB map was generated for the FS by interpolating the sediment data in the LDW (Figure 6). The map shows the high heterogeneity of sediment total PCBs, which can vary significantly within a short distance. The highest total PCB concentrations were found near the bank, which reflects the contributions of sources and high attachment of PCB to sediment. The FS report also presents the spatial distributions of arsenic, cPAHs, and dioxin/furans. They are all highly heterogeneous.

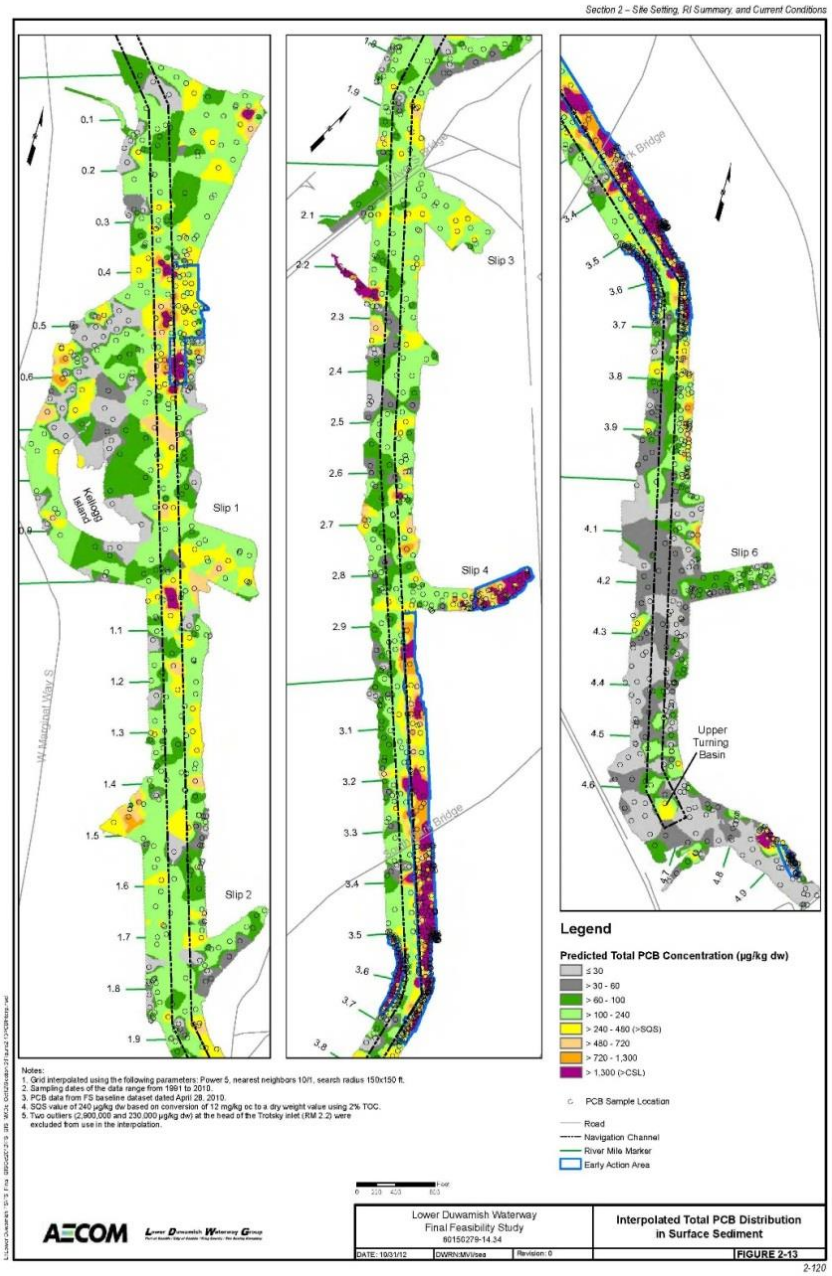

Figure 6. Interpolated spatial distribution of total PCBs in sediment of the LDW (2007)

For other COCs considered in the RI report, the available information can be summarized as follows:

- Arsenic is well characterized in the sediment and tissue similar to PCBs. However, more water column data are available for arsenic than PCBs. Hundreds of water samples of total and dissolved arsenic were collected in 1996-1997.
- PAHs and BEHP are also well characterized in LDW sediment and tissue, and had only limited data for surface water concentrations.
- Only 54 sediment samples and no surface water samples were available for dioxins/furans at the time of the RI.
- Mercury was detected in 746 out of 868 sediment samples and maps of the distribution of all metals in surface sediment are provided. The tissue analyses for mercury also appear to provide decent coverage. Only a small number of surface water samples had been analyzed for mercury. One important gap is that it does not appear that analyses were available for methylated mercury, which is the bioaccumulatable form.
- For all of the COCs other than metals, no pore water data were collected.

For the PLA effort, a new review of data coverage in the entire Duwamish Estuary corresponding to the proposed domain of the EFDC model was conducted to support a review of data gaps. Ecology's Sherlock and EIM databases were merged together first. Sherlock includes data collected in the LDW and associated with the RI/FS work. EIM is a more comprehensive database that includes data from throughout the watershed and collected for a variety of purposes. Surface sediment data and water column data were extracted from the merged databases for this effort. Surface sediment was defined as sampling taking place between 0 and 15 cm; sampling at depths in excess of 15 cm were excluded. For each of the eight candidate constituent groups, sampling locations and number of samples were reviewed and are presented below. When multiple samples were taken at a location during a given day (i.e., field duplicates), it was counted as a single sampling event. Surface sediment data were available beginning in 1980, but are summarized in this memorandum from 2000 through 2014. Spatially, sampling event counts are summarized for three sections of the proposed EFDC domain from upstream to downstream: Duwamish/Green RM 5.0 to 17.0, LDW RM 0.0 to 5.0, and East/West Waterways. Surface sediment data are also available extending into Elliott Bay. Appendix A and B provide generalized data plots by parameter from this data review. Surface sediment sampling locations are shown in Figure 7, Figure 8, and Figure 9, and water column sampling locations are shown in Figure 10.

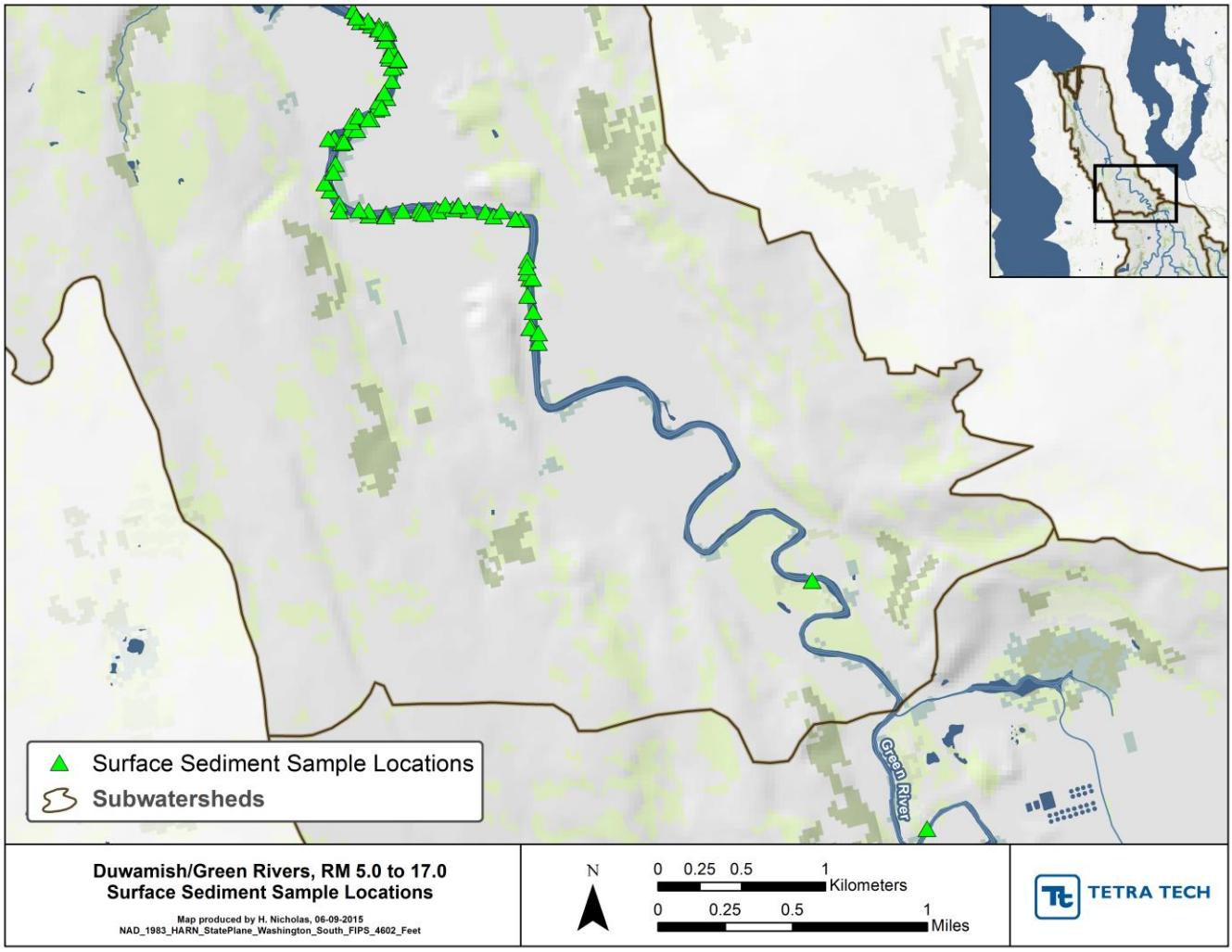

Figure 7. Surface sediment sampling sites in Duwamish/Green Rivers from RM 5.0 to 17.0

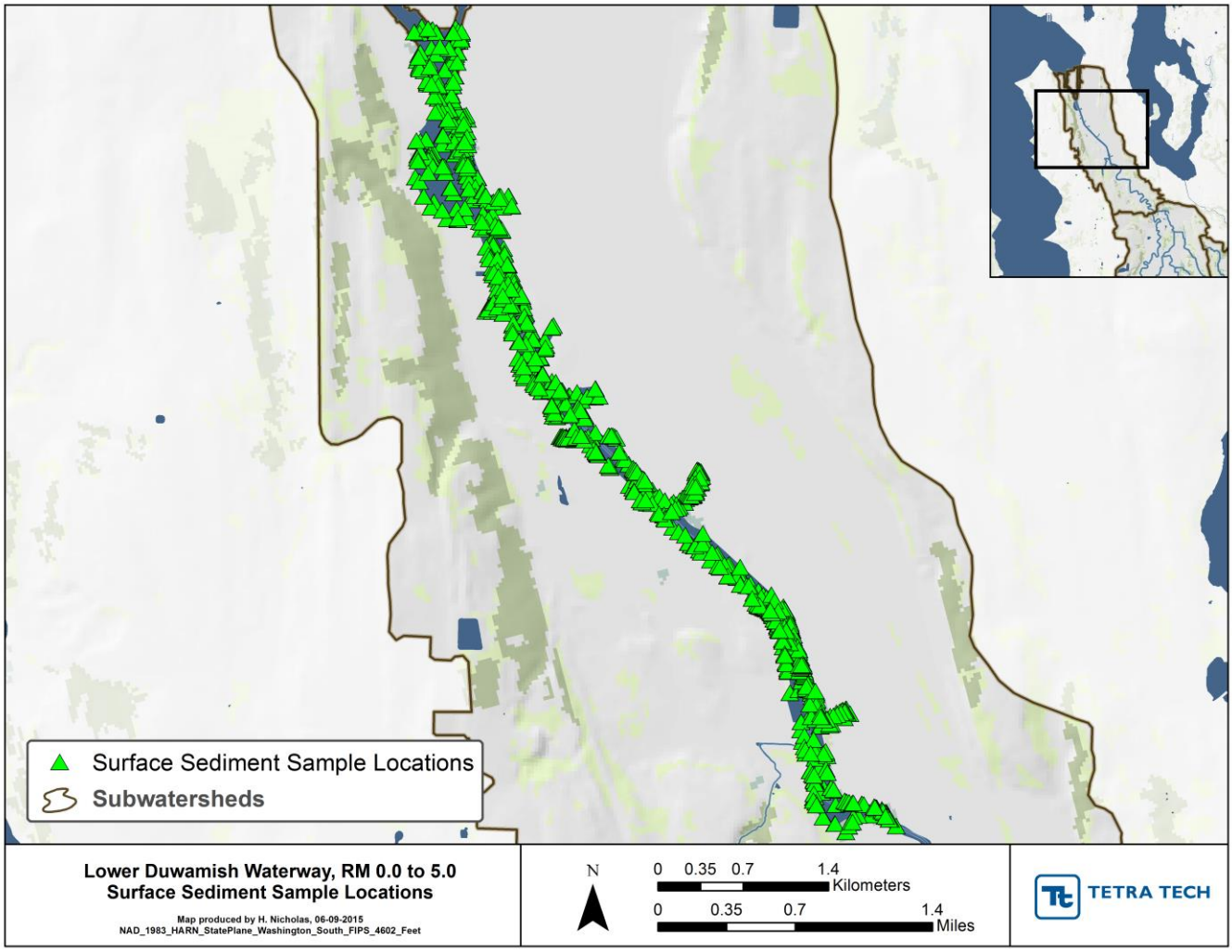

Figure 8. Surface sediment sampling sites in the LDW from RM 0.0 to 5.0

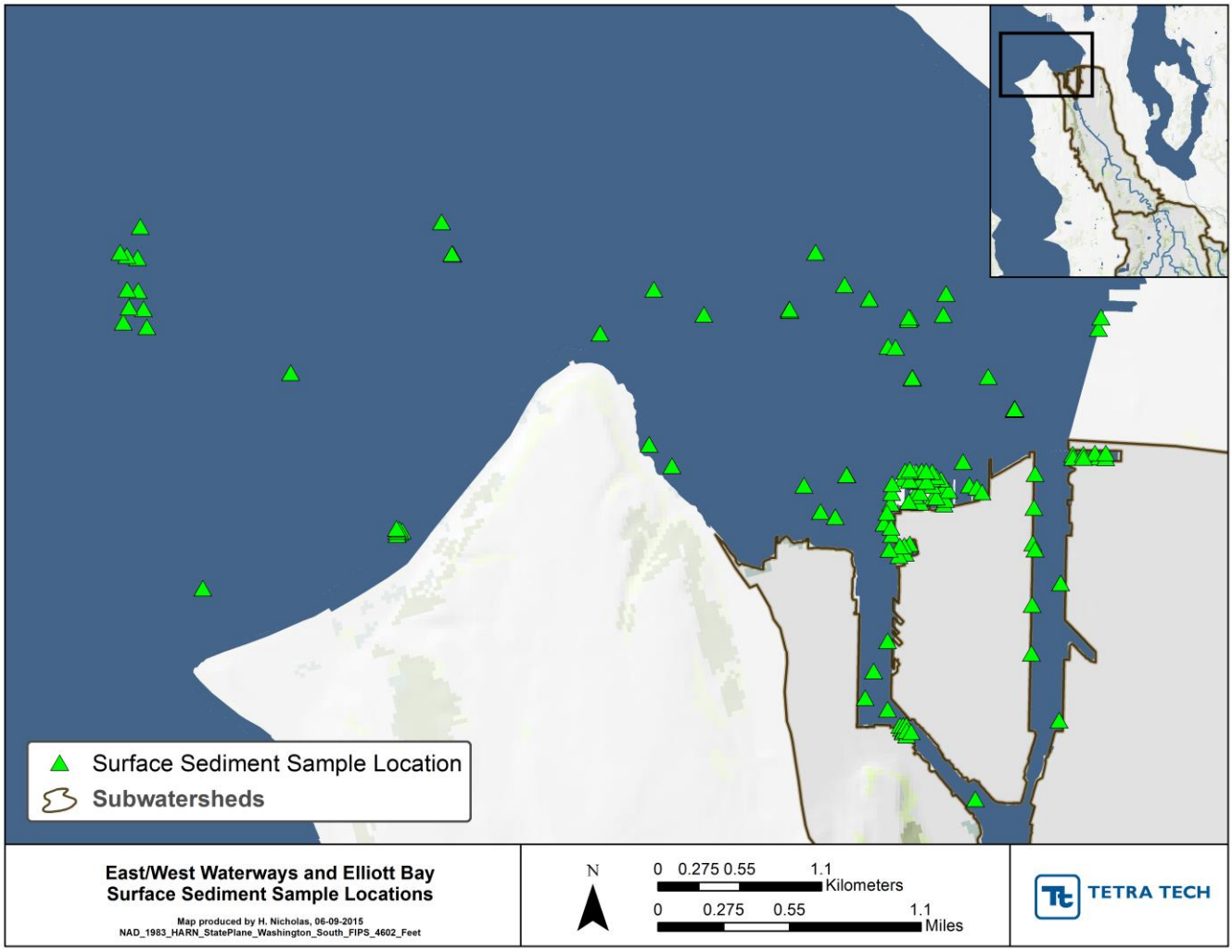

Figure 9. Surface sediment sampling sites in East/West Waterways and Elliott Bay

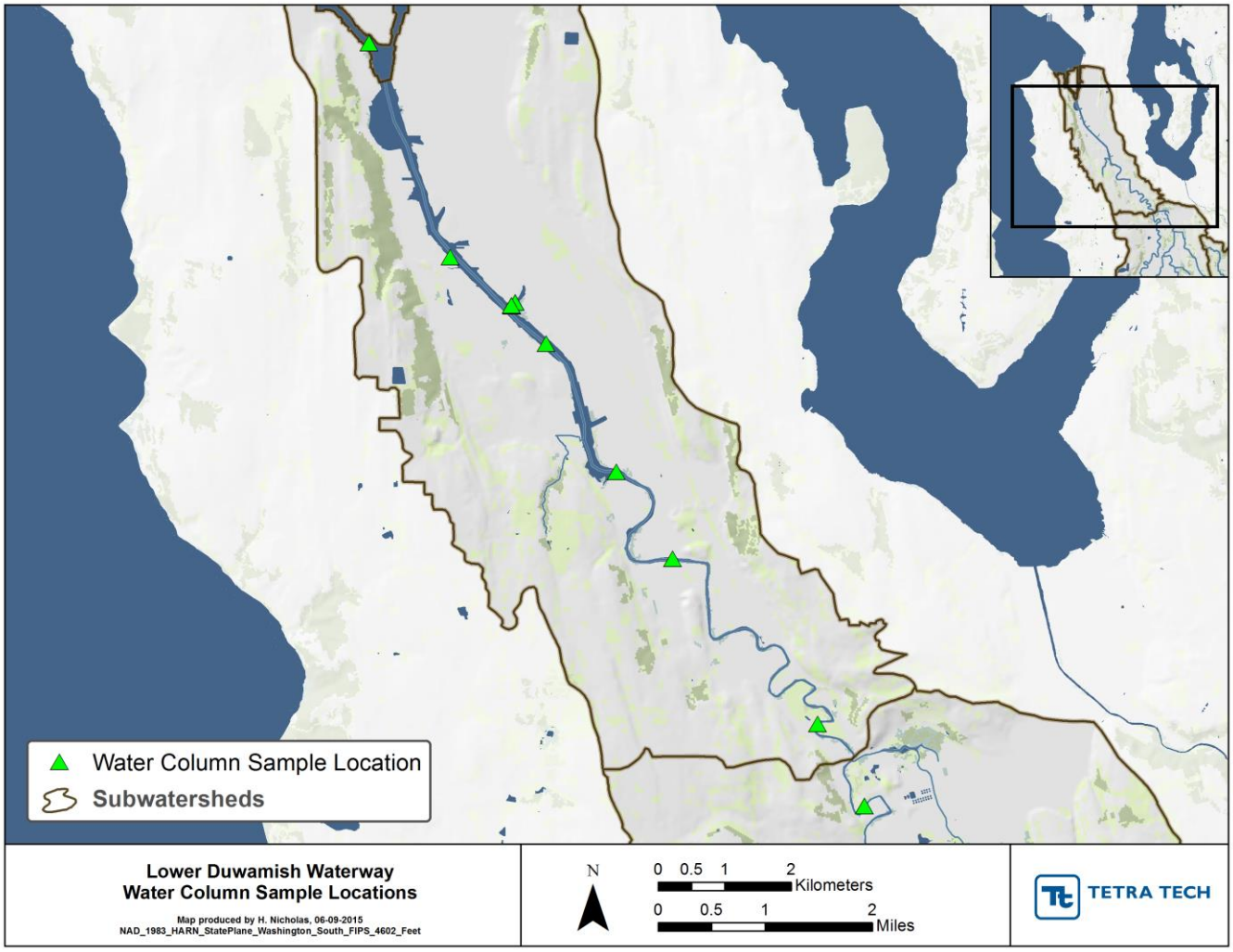

Figure 10. Water column sampling sites in the Duwamish Estuary

2.2.2.1 PCBs

Table 5 summarizes sampling event counts for the PCB data in the water column from the merged EIM and Sherlock databases. PCB homologs were calculated from the PCB congeners reported in the databases. PCB data were also measured as Aroclors in this area. Note that data are not available for 2006, 2009, 2010, and 2012. PCB congener data are most abundant in the upper portion in 2007. In the lower portion including LDW and the East/West Waterways, the data are limited with only 4 to 6 PCB sampling events available in 2005. PCB Aroclors were sampled at a similar frequency in the LDW (though during different years), but were sampled less frequently in the upstream part of the estuary, and not at all in the East and West Waterways.

Table 5. Water column PCB sampling events

Parameter	Location	2005	2007	2008	2011	2013	2014
PCB homolog 1	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 2	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	

Parameter	Location	2005	2007	2008	2011	2013	2014
PCB homolog 3	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 4	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 5	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 6	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 7	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 8	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 9	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB homolog 10	Duwamish/Green RM 5.0 to 17.0	4	16	2		5	
PCB-aroclor 1016	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1221	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1232	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1242	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1248	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1254	Duwamish/Green RM 5.0 to 17.0					5	1
PCB-aroclor 1260	Duwamish/Green RM 5.0 to 17.0					5	1
PCB homolog 1	LDW, RM 0.0 to 5.0	5					
PCB homolog 2	LDW, RM 0.0 to 5.0	5					
PCB homolog 3	LDW, RM 0.0 to 5.0	5					
PCB homolog 4	LDW, RM 0.0 to 5.0	5					
PCB homolog 5	LDW, RM 0.0 to 5.0	5					
PCB homolog 6	LDW, RM 0.0 to 5.0	5					
PCB homolog 7	LDW, RM 0.0 to 5.0	5					
PCB homolog 8	LDW, RM 0.0 to 5.0	5					
PCB homolog 9	LDW, RM 0.0 to 5.0	4					
PCB homolog 10	LDW, RM 0.0 to 5.0	4					
PCB-aroclor 1016	LDW, RM 0.0 to 5.0				6	1	1
PCB-aroclor 1221	LDW, RM 0.0 to 5.0				6	1	1

Parameter	Location	2005	2007	2008	2011	2013	2014
PCB-aroclor 1232	LDW, RM 0.0 to 5.0				6	1	1
PCB-aroclor 1242	LDW, RM 0.0 to 5.0				6	1	1
PCB-aroclor 1248	LDW, RM 0.0 to 5.0				6	1	1
PCB-aroclor 1254	LDW, RM 0.0 to 5.0				6	1	1
PCB-aroclor 1260	LDW, RM 0.0 to 5.0				6	1	1
PCB homolog 1	East/West Waterways	6					
PCB homolog 2	East/West Waterways	6					
PCB homolog 3	East/West Waterways	6					
PCB homolog 4	East/West Waterways	6					
PCB homolog 5	East/West Waterways	6					
PCB homolog 6	East/West Waterways	6					
PCB homolog 7	East/West Waterways	6					
PCB homolog 8	East/West Waterways	6					
PCB homolog 9	East/West Waterways	5					
PCB homolog 10	East/West Waterways	5					

Table 6 provides the PCB sampling event counts in the surface sediment from the merged databases from 2000 to 2014. PCB homologs were calculated from the PCB congeners. PCB data were also measured as Aroclors in this area. PCB data in surface sediment are more abundant compared to water column data. The sediment data are available at different locations in different years, which can provide useful information for the temporal change of PCB levels in the sediment. A more detailed data analysis at the EFDC model grid level will provide information on the spatial and temporal variations of surface sediment PCBs. In general, PCB Aroclors were monitored much more frequently than congeners in surface sediment. Aroclor monitoring is especially dense in the LDW, with nearly 1,500 sampling events spanning 2000 – 2014.

Table 6. Surface sediment PCB sampling events

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
PCB homolog 1	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 2	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 3	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 4	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 5	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 6	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 7	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 8	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 9	Duwamish/Green RM 5.0 to 17.0						4			7					6	
PCB homolog 10	Duwamish/Green						4			7					6	

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
	RM 5.0 to 17.0															
PCB-aroclor 1016	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1221	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1232	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1242	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1248	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1254	Duwamish/Green RM 5.0 to 17.0						10			74			2		7	
PCB-aroclor 1260	Duwamish/Green RM 5.0 to 17.0						10			73			2		7	
PCB homolog 1	LDW, RM 0.0 to 5.0						10									
PCB homolog 2	LDW, RM 0.0 to 5.0						10		3						3	
PCB homolog 3	LDW, RM 0.0 to 5.0						10		3						3	
PCB homolog 4	LDW, RM 0.0 to 5.0					26	72		3						3	
PCB homolog 5	LDW, RM 0.0 to 5.0					26	72		3						3	
PCB homolog 6	LDW, RM 0.0 to 5.0					26	72		3						3	

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
PCB homolog 7	LDW, RM 0.0 to 5.0					26	72		3						3	
PCB homolog 8	LDW, RM 0.0 to 5.0						10		3						3	
PCB homolog 9	LDW, RM 0.0 to 5.0						10		3						3	
PCB homolog 10	LDW, RM 0.0 to 5.0						10		3						3	
PCB-aroclor 1016	LDW, RM 0.0 to 5.0	18	4	18	64	261	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1221	LDW, RM 0.0 to 5.0	18	4	18	64	277	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1232	LDW, RM 0.0 to 5.0	18	4	18	64	277	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1242	LDW, RM 0.0 to 5.0	18	4	18	64	259	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1248	LDW, RM 0.0 to 5.0	18	4	18	64	277	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1254	LDW, RM 0.0 to 5.0	18	4	18	64	264	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1254/1260	LDW, RM 0.0 to 5.0					8										
PCB-aroclor 1260	LDW, RM 0.0 to 5.0	18	4	18	64	264	385	169	47	55	41	26	204	112	3	64
PCB-aroclor 1262	LDW, RM 0.0 to 5.0					16		61	3	27	7	3	19	9	3	64
PCB-aroclor 1268	LDW, RM 0.0 to 5.0					16		61	3	25	7	3	19	9	3	64

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
PCB homolog 1	East/West Waterways, Elliott Bay						4								5	
PCB homolog 2	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 3	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 4	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 5	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 6	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 7	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 8	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 9	East/West Waterways, Elliott Bay			1			4		12		4				21	
PCB homolog 10	East/West Waterways, Elliott Bay			1			4		12		4				21	

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
PCB-aroclor 1016	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1016/1242	East/West Waterways, Elliott Bay															
PCB-aroclor 1221	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1232	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1242	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1248	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1254	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1260	East/West Waterways, Elliott Bay	7	11	4		23	28		14		8		14	1	27	
PCB-aroclor 1262	East/West Waterways, Elliott Bay								12		8			1	16	
PCB-aroclor 1268	East/West Waterways, Elliott Bay								12		8			1	16	

2.2.2.2 cPAHs

cPAH data in the water column were collected during 2008, 2013, and 2014 (Table 7). Most of the water column data are available upstream of the LDW, and were collected mainly in 2008. Data in the LDW is minimal with only one sampling event each in 2013 and 2014 for five of the seven cPAH species of interest. No water column data are available for the East and West Waterways. The majority of samples are reported as being below detection limits.

Table 7. Water column cPAH sampling events

Parameter	Location	2008	2013	2014
Benz[a]anthracene	Duwamish/Green RM 5.0 to 17.0	18	5	1
Benzo(a)pyrene	Duwamish/Green RM 5.0 to 17.0	18	5	1
Benzo(b)fluoranthene	Duwamish/Green RM 5.0 to 17.0	18		
Benzo(k)fluoranthene	Duwamish/Green RM 5.0 to 17.0	18		
Chrysene	Duwamish/Green RM 5.0 to 17.0	18	5	1
Dibenzo(a,h)anthracene	Duwamish/Green RM 5.0 to 17.0	18	5	1
Indeno(1,2,3-cd)pyrene	Duwamish/Green RM 5.0 to 17.0	18	5	1
Benz[a]anthracene	LDW, RM 0.0 to 5.0		1	1
Benzo(a)pyrene	LDW, RM 0.0 to 5.0		1	1
Chrysene	LDW, RM 0.0 to 5.0		1	1
Dibenzo(a,h)anthracene	LDW, RM 0.0 to 5.0		1	1
Indeno(1,2,3-cd)pyrene	LDW, RM 0.0 to 5.0		1	1

Table 8 provides a summary of the cPAH sampling events in surface sediment. In the upper portion of the EFDC model domain, sediment cPAH data are limited temporally, but were sampled intensively during 2008. Surface sediment cPAH data were collected most frequently in the LDW, with good temporal coverage. Data were collected less frequently in the East/West Waterways and the Elliott Bay, but do show good temporal coverage. A more detailed data analysis at the EFDC model grid level will provide information on the spatial and temporal variations of surface sediment cPAHs.

Table 8. Surface sediment cPAH sampling events

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Benz[a]anthracene	Duwamish/Green RM 5.0 to 17.0						5			73			2		7
Benzo(a)pyrene	Duwamish/Green RM 5.0 to 17.0						9			73			2		7
Benzo(b)fluoranthene	Duwamish/Green RM 5.0 to 17.0						9			73					
Benzo(k)fluoranthene	Duwamish/Green RM 5.0 to 17.0						9			73					
Chrysene	Duwamish/Green RM 5.0 to 17.0						9			73			2		7
Dibenzo(a,h)anthracene	Duwamish/Green RM 5.0 to 17.0						9			73			2		7
Indeno(1,2,3-cd)pyrene	Duwamish/Green RM 5.0 to 17.0						9			72			2		7
Benz[a]anthracene	LDW, RM 0.0 to 5.0	12	2	1	27	90	184	126	33	36	35	23	204	96	3
Benzo(a)pyrene	LDW, RM 0.0 to 5.0	17	4	1	32	160	338	161	33	36	35	23	204	96	3
Benzo(b)fluoranthene	LDW, RM 0.0 to 5.0	17	3	1	32	151	338	161	33	34	35	23			3
Benzo(k)fluoranthene	LDW, RM 0.0 to 5.0	17	3	1	32	151	338	161	33	34	35	23			3
Chrysene	LDW, RM 0.0 to 5.0	17	4	1	32	156	338	161	33	36	35	23	204	96	3
Dibenzo(a,h)anthracene	LDW, RM 0.0 to 5.0	17	4	1	32	156	338	161	33	36	35	23	204	96	3

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Indeno(1,2,3-cd)pyrene	LDW, RM 0.0 to 5.0	17	4	1	32	156	338	161	33	36	35	23	204	96	3
Benz[a]anthracene	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Benzo(a)pyrene	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Benzo(b)fluoranthene	East/West Waterways, Elliott Bay		11	1			8		14		8			1	16
Benzo(k)fluoranthene	East/West Waterways, Elliott Bay		11	1			8		14		8			1	16
Chrysene	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Dibenzo(a,h)anthracene	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Indeno(1,2,3-cd)pyrene	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27

2.2.2.3 2,3,7,8-TCDD

The water column data for 2,3,7,8-TCDD are very limited with only six samples collected from the upper portion (one in 2007 and five in 2013).

Table 9 summarizes the 2,3,7,8-TCDD sampling events in the surface sediment. Data are not available for 2000 – 2004. Most of the sediment 2,3,7,8 -TCDD data were measured in the LDW with good temporal coverage. Data upstream and downstream of the LDW are limited.

Table 9. Surface sediment 2,3,7,8-TCDD sampling events

Location	2005	2006	2007	2008	2009	2010	2011	2012	2013
Duwamish/Green RM 5.0 to 17.0	1			27					6
LDW, RM 0.0 to 5.0	37	22	3	13	47	10	37	40	
East/West Waterways, Elliott Bay	2		19		4			1	10

2.2.2.4 DEHP

Table 10 shows the sampling events for DEHP in both the water column and surface sediment in the Duwamish Estuary. Water column data are very limited with only six sampling events in the upper portion in 2013 – 2014 and two sampling events in the LDW in 2013 – 2014. Surface sediment data were collected most frequently in the LDW with good temporal coverage. DEHP monitoring is limited temporally in the upper portion, but was intensively monitored in 2008. Data are somewhat limited in the East/West Waterways and Elliott Bay, but do show reasonable temporal coverage.

Table 10. Water column and surface sediment DEHP sampling events

Sample Type	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Water Column	Duwamish/Green RM 5.0 to 17.0														5	1
Water Column	LDW, RM 0.0 to 5.0														1	1
Surface Sediment	Duwamish/Green RM 5.0 to 17.0						9			40			2		7	
Surface Sediment	LDW, RM 0.0 to 5.0	17	4	1	32	160	338	161	33	34	29	20	204	96	3	
Surface Sediment	East/West Waterways, Elliott Bay	7	11	4		2	8		14		8		14	1	27	

2.2.2.5 Metals

Table 11 provides metals sampling event data in the water column. Both dissolved and total metals are available. However, the amount of data is very limited. No water column metals data are available prior to 2011 in the LDW, and no data are available at all for the East and West Waterways.

Table 11. Water column metals sampling events

Parameter	Location	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Dissolved Arsenic	Duwamish/Green RM 5.0 to 17.0	2	2	1	2							1
Dissolved Copper	Duwamish/Green RM 5.0 to 17.0	2	2	3	4	2	3					1
Dissolved Mercury	Duwamish/Green RM 5.0 to 17.0	2	2	1								1
Dissolved Zinc	Duwamish/Green RM 5.0 to 17.0	2	2	1	2							1
Total Arsenic	Duwamish/Green RM 5.0 to 17.0	2	2	1	2						7	1
Total Copper	Duwamish/Green RM 5.0 to 17.0	2	2	3	4	2	3				7	1
Total Mercury	Duwamish/Green RM 5.0 to 17.0	2	2	1	2						7	1
Total Zinc	Duwamish/Green RM 5.0 to 17.0	2	2	1	2						7	1
Dissolved Arsenic	LDW, RM 0.0 to 5.0								6	6	1	1
Dissolved Copper	LDW, RM 0.0 to 5.0								6	6	1	1
Dissolved Mercury	LDW, RM 0.0 to 5.0								6	6	1	1
Dissolved Zinc	LDW, RM 0.0 to 5.0								6	6	1	1
Total Arsenic	LDW, RM 0.0 to 5.0								6	6	1	1
Total Copper	LDW, RM 0.0 to 5.0								6	6	1	1
Total Mercury	LDW, RM 0.0 to 5.0								6	6	1	1
Total Zinc	LDW, RM 0.0 to								6	6	1	1

Parameter	Location	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
	5.0											

Table 12 provides total metals sampling event counts in surface sediment. The LDW has a significant amount of data, notably between 2003 to 2012. A more detailed data analysis at the EFDC model grid level will provide information on the spatial and temporal variations of metals in surface sediment in the LDW. Data are available less frequently in the Waterways and Elliott Bay, but show good temporal coverage. Data in the upper portion are limited, but were monitored intensively in 2008.

Table 12. Surface sediment metals sampling events

Parameter	Location	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Arsenic	Duwamish/Green RM 5.0 to 17.0						14			68			2		7
Copper	Duwamish/Green RM 5.0 to 17.0						9			41			2		7
Mercury	Duwamish/Green RM 5.0 to 17.0						9			41			2		7
Zinc	Duwamish/Green RM 5.0 to 17.0						9			41			2		7
Arsenic	LDW, RM 0.0 to 5.0	17	4	1	29	184	338	158	46	36	35	23	204	96	3
Copper	LDW, RM 0.0 to 5.0	17	4	1	29	184	338	158	33	34	29	20	204	96	3
Mercury	LDW, RM 0.0 to 5.0	6	4	1	29	234	338	159	33	36	29	20	204	96	3
Zinc	LDW, RM 0.0 to 5.0	15	4	1	29	184	338	158	33	34	29	20	204	96	3
Arsenic	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Copper	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27
Mercury	East/West Waterways, Elliott Bay	10	11	7		2	8		14		8		14	1	29
Zinc	East/West Waterways, Elliott Bay	7	11	5		2	8		14		8		14	1	27

In summary, water column data are limited for all the toxics. Water column data were collected most frequently in the upper portion from RM 5.0 to RM 17.0, and include all the parameters of interest. PCBs, cPAHs, and metals were collected in the LDW on a limited basis. PCB congener data were collected in the Waterways during 2005 only.

Surface sediment data were collected much more frequently than water column data in the Duwamish Estuary. For PCBs, Aroclor data are more numerous than congner/homolog data. The Aroclor data can provide information on the spatial and temporal trends of PCBs. However, they do not provide a fully reliable basis for specifying initial conditions and to support model calibration. cPAHs data were collected in the LDW extensively in multiple years, and to a lesser extent in the Waterways and Elliott Bay during multiple years. These data can support both development of initial conditions and model calibration. 2,3,7,8-TCDD data were also collected frequently in the LDW from 2005 to 2012. A more detailed analysis on the sampling locations will help to identify whether temporal and spatial variations can be extracted from these data. Sediment DEHP and metals data in the LDW were collected extensively during multiple years. Similar to the cPAHs, these data can be used to support the initial conditions and model calibration.

Water column concentrations of total PCBs, benz(a)anthracene, and dissolved and total metals from selected sites are presented in figures in Appendix A. These data represent locations where frequent monitoring took place during a relatively short time period. Total PCBs were calculated by summing up the individual PCB congeners. Total PCBs and benz(a)anthracene are from a site located on Lower Green River, while the metals are from a site in the LDW at RM 4.8. PCBs and benz(a)anthracene are generally at or near the detection limit most of the time, but show occasional elevated values. Both dissolved and total metal levels are at relatively stable levels at this LDW site. All of the metals values were reported above detection limits.

Longitudinal plots of concentrations of the parameters of interest in surface sediment in the LDW are shown in Appendix B (note that an outlier was omitted from most of the plots to allow for better visualization of the trends). From these plots, it can be seen that spatial variations are significant for all of the toxics and the highest values are observed at different locations, depending on the parameter. For instance, PCBs are elevated between RM 3.0 and 3.5. On the other hand, cPAHs tend to be the lowest between RM 3.0 and 3.5. 2,3,7,8 TCDD tends to be relatively low in most locations but shows high values at RM 1.4 and 2.2. DEHP is highest at RM 2.2. Locations of high metals values vary by parameter. Values reported below the detection limit occur at a high frequency for dibenzo(a,h)anthracene and DEHP. The other cPAHs have reported non-detects somewhat frequently, with the exception of benz(a)anthracene. 2,3,7,8 TCDD and mercury also have frequent non-detects. The remaining metals have only occasional non-detects. About 18% of the congener values contributing to the summed total PCB values were non-detects.

2.2.3 Data Types and Data Gap Filling Approaches

As discussed in the previous technical memorandum (Tetra Tech, 2015), three types of data including background, boundary conditions, and data to support calibration are used to support the EFDC model development. The background data for the EFDC model include shoreline and bathymetry for model segmentation, and initial toxics levels in the sediment bed for simulating sediment and toxic fate and transport. The boundary conditions provide external loadings of toxics to the model from all the sources. The data inside the model domain are used to support model calibration to identify the values of rates and constants that can represent the processes in the system realistically. In this memorandum, the focus is to identify the approaches for filling data gaps for suspended sediment and the toxics. Weather and flow data are not discussed here. In addition, the discussion here is based on the data account summary that was conducted for the technical approach (Tetra Tech, 2014) and the previous technical memorandum (Tetra Tech, 2015), and a summary of data from the merged Sherlock and EIM databases for data from 2000 to 2014. New data within the estuary that are not included in these databases have not been evaluated for the estuary. Detailed data filling approaches for specific toxics may change based on new information, modeling period, and a detailed data analysis; however, the general approach will remain the same.

2.2.3.1 Initial conditions

The EFDC model is a dynamic model which requires initial conditions to start the simulation. Initial conditions can also be considered as the net result of historical processes before the beginning time of the simulation. The initial conditions are required for the sediment and toxics in both water column and sediment layers of the model.

Water Column Initial Conditions

The suspended sediment concentration (SSC) and toxics concentration in the water column are highly variable in time due to variable freshwater flow and loading, as well as tidal influences in the Duwamish Estuary; however, they are not persistent. A short spin-up period (two or three months) can usually wash out the effect of initial water column concentrations. In practice, this means that the actual calibration period of the model begins a few months into the simulation. The SSC and toxics levels in the water column can be assigned to an initial low level because limited data are available for simulating a historical period. The boundary inflows and other inputs will replace the initial mass/energy assigned to the grid cell within a few months of simulation.

Sediment Layer Initial Conditions

The sediment and toxics levels in the sediment layer change much more slowly than those in the water column in the estuary. As a result, the initial condition of the sediments has a much longer memory than the water column. The initial conditions in the sediment layer will rely heavily on monitoring data. The results from existing sediment and toxics models from both King County and LDWG will also be used to provide supplementary data to support the determination of initial conditions in areas with limited monitoring or where monitored conditions are expected to have undergone significant changes. A spin-up period is expected to fill the gaps of missing data by running the model for an extended time period to build-up the initial condition for the model simulation.

Based on the data summary, data on potential toxics of concern in the sediment layer are available for the LDW and will be used as the basic data for determining the initial conditions in the LDW. The EFDC grid will be overlaid with the sampling data points and data within the same model cells will be summarized together to represent the cell level toxic concentrations. For portions of the model above RM 5.0 and below the LDW, the limited available data will be used to specify approximate initial conditions.

Most of the data for PCBs in the LDW were reported as Aroclors, which is a data gap relative to modeling PCB congeners or homologs. For other toxics, data can be used to generate initial levels in the sediment layer in LDW. Spatial interpolation is still needed as the sampling locations will not be able to cover all the EFDC model cells. For the rest of the Duwamish Estuary, limited data will be used to assign initial conditions. Due to the high heterogeneity of the toxics in sediment, a series of model runs may need to be conducted to test if the initial condition is reasonable.

The initial sediment layer condition including sediment layer thickness, porosity, and fractions of particle sizes will be based on a combination of the LDWG model results and monitoring data.

2.2.3.2 Boundary Conditions

The SSC, sediment, and toxics levels in the Duwamish Estuary and the lower portion of the Green River are influenced by mainly three types of boundary conditions including upstream boundary conditions, lateral boundary conditions, and downstream open boundary conditions. Direct air deposition to the water surface can also provide toxics to the system. Boundary conditions represent what brings into the EFDC model domain. For a dynamic model, the boundary conditions are time series of concentrations and loadings, preferably at daily scale. Below is a list of general approaches of data filling for time series.

- Linear interpolation for short term data gaps
- Monthly average and long-term values for long-term data gaps
- Regression

- Proven algorithms
- Derivations from other parameters
- Patching data from other stations
- Low concentration assumptions
- Existing models to fill gaps
- New LSPC model to fill gaps for pollutant loadings
- Calibration methods

The Green River above Kent, WA provides the upstream boundary conditions. The calibrated watershed model will provide boundary conditions to the EFDC model from the upstream Green River.

The lateral boundary conditions include flow and loadings from tributaries and direct drainage areas below the upstream boundary location, and the stormwater and CSOs from the surrounding areas of the Duwamish Estuary. Similar to the upstream boundary conditions, the watershed model will also provide the lateral boundary conditions except for CSOs. For the toxics, CSO sampling data from King County can be used to specify the concentrations of the modeled COCs and other relevant parameters.

For the downstream open boundary conditions, data are needed to provide the SSC and toxics levels outside of the Elliott Bay. During flood tide period, tidal current carries water into the estuary. When the levels of SSC and toxics are lower than those in the Duwamish Estuary, tide helps to dilute the SSC and toxics in the estuary. Turbidity data are available and turbidity data can be converted to SSC to be used as open boundary condition because SSC is usually a major contributor for turbidity (see Thackston and Palermo, 2006). Data are not available for other selected parameters as of this review. The Elliott Bay waterfront recontamination study collected some data near Pier 48 to Pier 59. Sediment data were collected at the study area. These data, however, cannot be used as open boundary condition because they are located within the model domain while open boundary condition should be the condition outside of the model domain. It is planned to use low level concentration assumptions and data from elsewhere in Puget Sound to specify the open water boundary unless data are available in the sound.

In addition to the loadings from the drainage areas and CSOs, air deposition can contribute toxics to the EFDC model domain. The total mass of air deposition depends on the surface area of the water body. Outside of the water surface, air deposition contribution to loading is through the rainfall-runoff processes and will be included in the watershed model. Air deposition fluxes vary spatially. Table 13 is extracted from the data summary of Task 4.1 (Tetra Tech, 2015), and it shows the data amount for air deposition over the Duwamish Estuary. No data are available for SSC, organic carbon, and phthalates. For other parameters, limited data are available. New data (based on studies described later in this memo in the Watershed section) provide more information on the range of the air deposition fluxes. A sensitivity analysis can also be used to evaluate the model responses to air deposition.

Table 13. Air deposition data in the Duwamish Estuary (from Task 4.1 summary)

Parameters	Air Deposition	
	Stations	Samples
TSS	0	0
Organic Carbon	0	0
Total Organic Carbon	0	0
PCBs	3	25
PAHs	3	73

Parameters	Air Deposition	
	Stations	Samples
Dioxin/Furan	3	26
Arsenic	3	72
Phthalates	0	0
Copper	3	72
Zinc	3	72
Mercury	3	72

2.2.3.3 Data to Support Calibration

A numerical model is essentially a set of mathematical equations (governing equations) that describe how water moves, and how material moves and reacts in the water and sediment layer. Governing equations include rates and coefficients that describe the processes of adsorption-desorption, diffusion, decomposition, and volatilization. These rates and coefficients need to be determined so that the model can simulate these processes. For water quality modeling, model calibration is used to refine these rates and coefficients through running the model iteratively and adjusted as necessary. During the iteration, model results will be compared against observation data until model results agree well with data. Initial estimates of rates and coefficients will be based on a combination of site-specific data and literature. Results will be check for reasonableness. If the rates and coefficients are outside of the normal ranges of the literature values, a further investigation will be conducted to determine reasons.

The needs of data to support model calibration are different from the data for model configuration. Without data to support configuration, a model cannot be constructed. Without data for calibration, a model still can run, without knowing if the results are robust or not. The observed data in the water column and sediment layer are used to evaluate model performance and guide the adjustment of rates and coefficients. The model robustness is positively correlated with the amount of data.

For the Duwamish Estuary including the LDW, the data to support calibration and the data for initial condition are from the same pool. Depending on the simulation period, some of the data will be used for initial conditions, and others will be used for calibration. Tables in Section 2.2.2 show the availability of the data by year for both water column and sediment data. While spatial distributions at a chosen time period are critical in assigning initial conditions, calibration will look spatial and temporal trends of concentrations in response to the loadings.

Data in the water column are limited for all of the toxics. In surface sediments, PCB congener/homolog data are also limited. For the remaining toxics in surface sediment, data coverage is fair to good based on the counts shown in the tables in Section 3.2.2.

2.2.4 CSOs

Stormwater in the area immediately adjacent to the LDW is served by a complex mix of combined sewers and separate storm sewers. Runoff from approximately 61% of the drainage area of the Duwamish Estuary enters the pipe network of CSOs. The estimation of annual total discharge to the estuary is 75 MG/yr from CSOs. Even though the drainage area of CSOs is larger than those for the direct stormwater discharge, the total flow from CSOs is much lower than that of direct stormwater discharge (estimated at 4,000 MG/yr).

Records of CSO discharge volumes are available, as are concentration data in solids and in whole water that are representative of CSOs. Hydrologic and hydraulic models for the combined sewer are also available, and provide a basis for estimating future flows. Figure 11 shows the King County CSO areas and the corresponding computer models. Table **14** lists the locations of the CSOs and the models used at these areas.

Figure 11. Computer models used for CSOs (including non-Duwamish Estuary related areas, from King County 2012 Long Term CSO Control Plan: Appendix B Hydraulic Modeling Update and Evaluations)

Table 14**. CSO locations and associated models**

Location	Hydrologic/Hydraulic Model
Terminal 115 (LDW)	MOUSE
Chelan (West Waterway)	Runoff/Transport
S Michigan (LDW)	MOUSE
Brandon (LDW)	MOUSE
Hanford2 (East Waterway)	Runoff/Transport
Kingdome (Elliott Bay)	MOUSE

Location	Hydrologic/Hydraulic Model
King (Elliott Bay)	MOUSE
Lander (East Waterway)	Runoff/Transport
Rainier PS	MOUSE
Bayview	MOUSE
Hanford @ Rainier	MOUSE
West Michigan (LDW)	MOUSE
Balance of North Interceptor	Runoff/Transport

Note: Tt attempted to remove locations not related to the Duwamish Estuary, but some may remain in the above list.

Since the models were used for the 2012 Long term CSO Control Plan, the model configurations are up to date including the pipes, pumps, flow regulators, as well as the sanitary sewer system. When the model simulation period is defined, these models can be updated with new precipitation data to simulate the overflow rates.

For both the separate and combined sewer systems it is believed that the majority of the COCs, which are strongly sorbed, are likely to be associated with suspended sediment or solids loads derived from surface erosion on pervious land and from build-up/wash-off on impervious covers. The models thus need to accurately simulate solids loading in stormwater. This is an integral function of the LSPC/HSPF simulations of surface runoff, and that information can also be used to provide input to the stormwater component of the combined sewer system. Assigning pollutant loads to the solids inputs is a much greater challenge due to the highly heterogeneous nature of localized contamination in the industrial corridor along the LDW. There are ongoing source investigations for many of these areas, but it will be a challenge to incorporate all this information into the watershed models.

Determination of contaminant concentrations and loads is even more challenging because flow in the combined sewer is a continuously varying mix of stormwater and sanitary sewage. King County collected CSO whole water data including temperature, conductivity, TSS, DEHP, and TOC at several locations covering the period from 1995 to 1998. CSO data from the EIM database include the following COCs at detectable levels:

- Benz[a]anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene
- Dibenzo(a,h)anthracene
- Indeno(1,2,3-cd)pyrene
- Di(2-ethylhexyl) phthalate
- Total Arsenic
- Total Copper
- Total Mercury
- Total Zinc

Analyses were also done for PCBs in whole water samples from CSOs, but all results were reported as not detected, likely due to detection limits. Later CSO sampling conducted in 2007-2010 (King Co., 2011) reported low-level results for all the COCs, including PCB and dioxin congeners. For both the separate sewer and the combined sewer system, the RI discusses data collected from in-line solids traps, which will be valuable for

specifying potency in specific sewer drainage areas, including data from 245 catch basins sampled between 2002 and 2007. Significant amounts of additional solids trap data have been collected since 2007.

Two options are available to estimate COC concentrations in the CSOs. One is to directly use a central tendency value of the collected data to represent an average condition of toxics in CSOs. This approach is easy to conduct. However, it does not provide a linkage between source and the concentration and it will be challenging to run management scenarios.

The other option is to use combined model and data to derive the concentrations based on the simulated mixing ratio of stormwater and sanitary sewage. The land processes for the stormwater discharge and for the runoff entering the CSO system are the same. The watershed model LSPC can be used to simulate the erosion of soil and wash-off of toxics from land surfaces into the combined sewer. With the calibrated LSPC land processes, the concentrations in the toxics in urban stormwater can be estimated. The toxics in sanitary sewage would be assumed to be at constant levels based on monitoring data. The mixing ratio information needs to be extracted from the CSO models that King County uses for the long term CSO control plan.

This approach would make maximal use of monitoring data, but also adds to the complexity of the model. In addition to the monitoring data for the CSOs, the stormwater monitoring data can also be used to best estimate the toxics in the runoff entering the CSO system. With the combined LSPC and CSO models, the sources and concentrations of toxics are linked together. Changes in land management or remediation of contaminated sites can be represented in LSPC and the corresponding change of toxics can be estimated. It should be noted that this approach will need to be re-visited after the detailed information from the King County CSO models become available.

2.2.5 Summary of Gaps and Strategies – EFDC Model

There is a substantial body of information available with which to construct or revise and calibrate an EFDC model of the Duwamish Estuary, including existing EFDC modeling efforts. Flow and sediment transport model applications are already available and additional data can be used to further refine the modeling. Significant amounts of information on bulk concentrations of COCs are available for the sediment but only more limited data are available for the water column. Limited or no pore water data are available, depending on the COC. These constitute data gaps for model development; however, it may not be easy to fill these gaps as the ideal data set would contain spatially and temporally contemporaneous measurements of concentrations in all media. This could perhaps be addressed during the remedial implementation phase of the CERCLA action on the site.

Some of the primary gaps related to the EFDC modeling of toxics in the Duwamish Estuary can be better characterized as knowledge gaps than data gaps. Specifically, data are not generally available for site-specific determination of kinetic parameters that control sorption to sediment and organic carbon, volatilization, mass transfer from the sediment to water, and solubility of organic pollutants can be considered as knowledge gaps.

All of these parameters can be estimated from values reported in the literature (e.g., solids partitioning can be estimated from octanol-water partition coefficients); however, there is plentiful evidence that behavior at specific sites can be quite variable due to factors such as the nature of inorganic carbon in the system, non-equilibrium processes, and partitioning to dissolved organic carbon.

Site-specific estimation of kinetic parameters could be pursued through additional field experiments, although this would be time-consuming and costly. Model calibration will also provide evidence as to the adequacy of assumptions based on literature. We recommend that the best approach will to be to develop the toxics model with available data and then conduct sensitivity analyses to determine the influence of parameter uncertainty on model results relevant to decision makers. In this way, the model can provide importance guidance as to the need for new data collection, following which the model calibration can be fine-tuned.

An additional key challenge is present in defining the CSO and lateral loads of COCs to the LDW. Tools are or will be available to estimate flows and solids loads from both CSOs and lateral separate storm sewer drainage to the LDW; however, the challenge will be in making appropriate use of the wealth of source information and a determination will need to be made as to the appropriate level of effort. The simple option would be estimate CSO loads from flow and central tendency of concentration data and to estimate separate storm sewer loads based on simulated flow, sediment transport, and "typical" storm solids concentration data. That approach, however, would not recognize the extensive work that has been done to identify specific source areas, nor would it recognize the changes that have taken place over time as various upland source control actions have been undertaken. Tasks and data needs for a more sophisticated analysis include the following, which is similar to the approach Tetra Tech developed for the Louisville (KY) Beargrass Creek CSO area TMDL models (Tetra Tech, 2008):

- Summarize and extract information from source control investigations, including estimated changes in source solids potency for COCs following remedial activities.
- Implement watershed model to estimate loading associated with the movement of suspended sediment and associated contaminants at a fine spatial scale. This may require constructing the model in a way that changes in sediment potency over time in response to remedial actions can be simulated. (Dissolved phase loads will also be evaluated.)
- Obtain complete spatial coverage of separate storm sewer and combined sewer drainages.
- Analyze existing CSO models to develop a complete time series of overflow events and mixing ratios of sanitary sewage and stormwater during those events.
- Obtain information on baseline concentrations of COCs in sanitary sewage.
- Construct time series of CSO concentrations of COCs based on the mixing ratios and stormwater concentration data.
- Perform detailed calibration of separate storm sewer loads. Flow and suspended sediment loads will be provided by the calibrated watershed model. The primary effort will be an accurate representation of source strengths. This can be evaluated based on measured in-line solids trap data and any whole water sampling performed as part of the source control investigations.
- Perform detailed calibration of CSO loads based on measured discharge concentrations and in-line solids trap data.

Table 15 summarizes data and knowledge gaps and options for the EFDC model.

Table 15. Summary of data, knowledge gaps and options for EFDC model

Data and Knowledge Gap	Options and Recommendations
In general, data are available but limited in some media. Data gaps and knowledge gaps exist for initial, boundary, and calibration data.	Options: 1. Use all available information including data and previous models to develop a model now of recent historic conditions. 2. Collect additional data and delay modeling to the future. Data collection needs to be coordinated to obtain initial, boundary, and calibration data sets in all media. Recommendation: Start developing and calibrating the model with available data and use model to guide needs for new data collection.

Data and Knowledge Gap	Options and Recommendations
Limited data for assigning initial conditions in the water column for all toxics	Options: 1. Assign low levels of initial toxics and equilibrate with sediment using a model spin-up period. 2. Collect data if the modeling period is in the future. Recommendation: Use model spin-up combined with existing data; test sensitivity of model results to this assignment. We anticipate low sensitivity to initial conditions in the water column.
Data for sediment initial conditions (depending on the modeling period) and need to account for remedial actions over time.	Options: 1. Rely on existing data and use previous model results if modeling a historical period. 2. Collect new data if the modeling period is in the future. Recommendation: It is unlikely that the massive characterization effort for sediment conditions undertaken in the RI can be repeated. The PLA model should thus rely on existing sediment data, but also needs to account for interim remedial actions over time. Applying the model to multiple years can be used to test simulated responses to remedial actions. In addition, use long model spin-up time and conduct multiple model tests.
SSC and toxic loadings from upstream	Options: 1. Use watershed model results for modeling a historical period. 2. Continue collection of comprehensive toxics data from the watershed and develop the model in the future. Recommendation: Existing HSPF models are calibrated for flow and sediment. Develop the upstream loading with a combination of these models and existing data; continue collection of new data to fill knowledge gaps for LSPC simulation.
SSC and toxics loadings from CSOs	Options: 1. Use existing CSO monitoring data and event volume modeling combined with best estimates of pollutant concentrations. 2. Combine CSO model and monitoring data with watershed model simulations of surface stormwater-derived loads. Recommendation: Use CSO model to develop time series of mixing ratios and estimate CSO concentrations based on fractions of stormwater and sanitary sewage. Use HSPF/LSPC to estimate stormwater concentrations and monitoring data for sanitary sewage concentrations. Confirm model performance relative to CSO outfall monitoring.
Limited toxics data in the water column; lack of information to do site-specific evaluation of some kinetic parameters such as partition coefficients.	Options: 1. Use available data and literature to approximate kinetic parameters. 2. Collect new field data to gain knowledge. 3. Conduct laboratory experiments to fill knowledge gaps.

Data and Knowledge Gap	Options and Recommendations
	4. Conduct literature review to fill knowledge gaps. 5. Conduct model sensitivity and uncertainty analyses to fill knowledge gaps. 6. Collect synoptic data for a modeling period in the future and delay model implementation. Recommendation: Develop model beginning with available data. Options 1 to 5 can all be potentially used to further constrain the data and knowledge gaps the model based on resource availability. Initial model development will greatly assist in determining the cost:benefit ratio of specific types of data collection.

2.3 LOWER DUWAMISH WATERWAY – FOOD WEB

2.3.1 Summary of LDW Food Web Model

The Food Web Model (FWM) for the LDW is an Arnot and Gobas model of steady-state PCB distribution in biota. Model documentation is included as Appendix D to the LDW RI report.

The FWM includes compartments for phytoplankton, zooplankton, filter-feeding benthic invertebrates, other benthic invertebrates (scavenger/predator/detritovore), and fish at several trophic levels. Data from the LDW for target species in many of these compartments were available except for the lowest trophic levels (phytoplankton, zooplankton). Benthic invertebrates were represented by a single scavenger/predator/detritovore compartment. The specific target species used in the FWM for the LDW, in order of declining trophic level, are English sole, Pacific staghorn sculpin, shiner surfperch, Dungeness crabs, slender crabs, and large clams.

Model building and calibration focused on averages over the whole LDW and used 190 composite tissue samples collected between 1997 and 2005. Water column data comes from the 2009 update of the 1999 King County EFDC model, documented as Attachment A to Appendix D of the RI report.

Interestingly, the FWM considers three phase partitioning in the water column (but not sediment), including partitioning to dissolved organic carbon. The model takes as input total PCB concentrations in the water column then calculates fractions based on partition coefficients, although only a single partition coefficient to organic carbon is entered by the user.

The model requires body weights and lipid content for individuals in each trophic level, and these were based on site data. The model also requires octanol-water partition coefficients (K_{ow}) within benthic invertebrate tissue. To address total PCBs, this was calculated as a weighted average over the set of congeners observed in invertebrate tissue samples and using the laboratory K_{ow} values in Hawker and Connell (1988). Diet for each trophic level combined literature information and gut content analysis with sensitivity addressed through multiple scenarios. The model was fit probabilistically through Monte Carlo simulation followed by identification of a best-fit model parameter set. The best-fit set had a mean across species of SPAF = 1.2, where SPAF is the ratio of modeled to observed tissue concentration when the modeled concentration is larger and the inverse of this ratio when the modeled concentration is lower.

Extensive sensitivity analysis found that tissue concentrations in all species are most strongly influenced by the water column concentration, K_{ow}, and the density of lipids. The water column PCB concentration primarily affects species that have food chain pathways that contain 25% or more zooplankton in their diet. Benthic invertebrate-specific parameters of body weight, relative fraction of pore water ventilated, and dietary absorption efficiency

also had relatively significant influences on results in many species. Correct assignment of dietary pathways is obviously important to the overall result and was the main factor adjusted as part of the Monte Carlo calibration approach. Additional data to further constrain estimates of dietary sources of individual species would be useful.

The report describes two other important sources of uncertainty in model specifications and parameters:

- Observed PCB tissue concentration data for individual species tended to be highly variable. The report cites analytical variability as a potential cause, but dynamic processes related to seasonal changes in feeding, depuration at spawning, and other causes that cannot be well addressed in a steady-state model may also be important.
- The fact that data from different media are not concurrent is a significant contributor to uncertainty. Much of the sediment data is from the late 1990s, and the baseline sediment distribution is for pre-dredging conditions, whereas the water column data were collected after dredging that occurred in 2003/2004 in the Duwamish/Diagonal area.

Performance of the model was further tested by comparing results for tissue data collected in 2007, although this as noted as not a "true validation test" because concurrent inputs for sediment and water column concentrations for 2007 were not available. The 2007 tissue results were lower than those observed in the calibration data and the FWM over-predicted the 2007 results, possibly because there were not matched input data on water and sediment concentrations for this year.

The FWM experience highlights the difficulties of applying a steady-state equilibrium model to what is clearly a rather dynamic system. Determining whether the model is performing adequately is particularly difficult when concurrent data in tissue, sediment, and water are not available.

The FWM has not been developed for other COCs beyond PCBs in the LDW. The basic Arnot-Gobas model is, however, applicable to most hydrophobic/lipophilic organic chemicals, including the additional prioritized parameters for the PLA in addition to PCBs: TCDD, PAHs, and DEHP. The formulation is not applicable to methylmercury, which bioconcentrates, but is primarily associated with viscera and muscle, rather than lipids. Bioaccumulation modeling is not proposed for arsenic and copper.

EIM currently contains a significant number of tissue samples for DEHP and CPAHs (~100), but less than half the number available for PCBs. Tissue data for 2,3,7,8-TCDD are currently very limited (only 3 samples for the estuary were found), although additional data may become available

2.3.2 Summary of Gaps and Strategies - FWM

The Arnot-Gobas model construct is applicable to evaluation of steady-state tissue concentrations of non-polar organic chemicals in the study area; however, the experience of application of the FWM to 2007 fish data suggests limitations to the analysis. A key issue is the lack of concurrent data for different compartments in a system where the sediment concentrations and, especially, the water column concentrations are changing over time. While new tissue data are being collected it will be necessary to rely in large part on older sediment data within the LDW. Some adjustments will need to be made to account for both interim remedial actions and possible dilution of surface sediment concentrations by continued deposition of cleaner sediment from the Green River. Temporal variability in water column concentrations can be addressed to some extent by the development of an improved water column model that simulates the responses to varying flow and loading conditions over time. Obtaining additional data on dietary sources of individual species would likely improve the model performance, but the steady state approximation is likely to continue to provide only an approximation of concentrations observed in tissue samples.

The previous FWM approach of evaluating bioaccumulation of total PCBs using a wide range of K_{OW} and other kinetic characteristics could be improved by an evaluation based on several homolog groups.

The Arnot-Gobas modeling framework should also be appropriate for TCDD, DEHP, and cPAHs; however, previous efforts with the FWM have not addressed these contaminants so it is difficult to predict how successful such an effort will be for the Duwamish. Bioaccumulation of these contaminants has, however, been successfully modeled elsewhere with the Arnot-Gobas framework. Very little tissue data for dioxins is currently available in EIM, so there may be limited capacity for calibrating bioaccumulation for this contaminant class. Instead, a bioaccumulation model for carcinogenic dioxins would likely be an unconfirmed estimate based on chemical characteristics relative to similar PCBs. Such an analysis would be useful based on currently available data; however, a fully supported analysis based on local conditions would require collection of several years of contemporaneous data on dioxin concentrations in fish (at multiple trophic levels), sediment, and water.

Predicting tissue accumulation of metals and the metalloid arsenic would require different modeling tools, such as DYMBAM. Our recommendation is that arsenic, copper, and/or zinc are best addressed based on water column concentrations and that tissue accumulation models are not needed for these constituents. As to mercury, a full treatment of tissue bioconcentration of methyl mercury requires specialized modeling tools. Data are not, however, available for methyl mercury concentrations in the environment nor for various environmental parameters that affect mercury methylation rates. Therefore, we also recommend that simulation of tissue concentrations of mercury not be pursued at this time. Additional sampling and analyses would be required if this is desired in the future. Existing data are likely sufficient to establish a mass balance modeling representation of total mercury in the water column.

Table 16 summarizes knowledge gaps and options for the FWM.

Table 16. Summary of knowledge gaps and options for Food Web Model

Knowledge Gap	Options and Recommendations
Lack of contemporaneous data in all media and biota	Options: 1. Conduct comprehensive new round of synoptic data in all compartments 2. Use models to estimate temporal changes in stores Recommendation: Option 2 is recommended despite being suboptimal due to the large cost of new comprehensive surveys.
Limited information on dietary sources of individual species	Options: 3. Conduct gut content surveys 4. Rely on existing data Recommendation: Rely on existing data (2), but supplement prior FWM effort by soliciting additional information from wildlife and university sources.
Limited tissue and exposure data for dioxins/furans	Options: 3. Collect additional data 4. Perform modeling based on limited extant data 5. Do not model dioxins/furans at this time Recommendation: Based on the contaminant-specific analyses, do not apply FWM to dioxins/furans at this time.
Lack of environmental exposure data for methylmercury	Options: 1. Collect additional data to characterize methylmercury exposure

Knowledge Gap	Options and Recommendations
	2. Simulate based on approximations from total mercury Recommendation: Do not pursue FWM simulation of mercury at this time.
Limited modeling tools for evaluating bioaccumulation of arsenic, copper, and zinc; limited data on factors controlling bioavailability	Options: 3. Do not model bioaccumulation of metals 4. Use DYMBAM model for bioaccumulation of metals Recommendation: Base analysis for these constituents on ambient WQS for protection of aquatic life rather than bioaccumulation models. Do not implement DYMBAM.

3.0 GREEN/DUWAMISH RIVER WATERSHED

In the PLA Technical Approach, a conceptual model was developed to help understand the issues and processes that must be considered to select a modeling platform. The PLA requires a source-response linkage and the estimation of existing loadings and target loadings to attain goals, as well as the distribution of those loads among sources and pathways to inform source reductions. As part of the linked modeling system, the watershed model, using the LSPC framework, not only includes the physical and chemical processes within the Green/Duwamish River watershed itself, but also integrates with the LDW by supplying inputs of hydrology, suspended sediment, and pollutants representing upstream sources.

The LSPC model, proposed for the watershed modeling tool, is a comprehensive watershed hydrology/loading model and uses a one-dimensional channel. The model includes hydrological and chemical/sediment loading simulation to predict chemical fate and transport on a basin scale based on a network of subwatersheds and stream reaches. The model can generate either hourly results or daily average results to predict and compare the modeled outcome with the existing observed data and/or to further utilize the results for advanced management decision support.

In previous work to support the PLA (Tetra Tech, 2014 and 2015), discussions were provided about available data and models for watershed model configuration and calibration. This included information for boundary forcing data such as meteorology, inflows, temperature, and constituent assignments at the upstream boundary of the model. The memo also discussed supporting data for the hydrology portion of the model. This includes, for example, flow data to calibrate hydrologic parameters. As suggested in this previous review and also based on the previous HSPF flow calibration that has been conducted by Aqua Terra and King County, the meteorological forcings, inflows, and overall flow data are considered sufficient for these portions of model development, therefore, no additional review was conducted for the present memo. Instead, the following sections focus on water quality-relevant data for characterizing sources of pollutants including point sources, atmospheric deposition, and runoff-based sources and pathways for the watershed model. The objective is to discuss where data or knowledge gaps may exist in the context of model construction and source attribution.

3.1 WATERSHED SOURCES AND PATHWAYS

A key function of the watershed model is to develop an estimate consistent with available monitoring data of sources of pollutant loads and their link to receiving streams loads. Watershed-based sources and pathways described in the Technical Approach include:

- Urban runoff and associated loads (of solids and pollutants),
- Agricultural runoff and associated loads,

- Other runoff such as from natural areas and associated loads,
- Atmospheric deposition, including spatial variation in deposition rates,
- Point source discharges (industrial, regulated stormwater outfalls, etc.),
- Spills and/or leaks (contaminated sites and industrial operations areas contributing high contaminant loads),
- Legacy COCs in bed sediments above the LDW, and
- Groundwater contributions to both watershed-based streams and to the LDW directly.

To address the question of whether there is enough data to create a credible source-response linkage model, we pose the following questions:

- What do we know about sources in the watershed?
- What information do we have to characterize these sources in the modeling environment?
- Are there sufficient data for calibration for specific COCs?

An analysis using this framework then forms the basis for determining what gaps exist and how important those gaps are, as well as a discussion of how to address them.

Data available to characterize sources, constrain model parameters, and calibrate pollutants within the model is discussed in the following sections of the memo. But first discussion is provided on key components of watershed model setup, calibration, validation since an understanding of linkages to the data needed to support these components will be useful.

3.2 WATERSHED MODEL DEVELOPMENT

Pollutant loads are delivered to tributaries via surface runoff, subsurface flows, groundwater flows, direct point source discharges, and other pathways. LSPC provides mechanisms for representing all these various pathways of pollutant delivery. The LSPC model implements the same algorithms present in the HSPF model; therefore, work that has already been done to calibrate the King County HSPF models should also apply to the revised watershed models. After initially configuring the watershed model, previously calibrated model parameters for hydrology will be evaluated through both calibration and validation tests. Calibration is an iterative procedure of parameter evaluation and refinement as a result of comparing simulated and observed values of interest. It is required for parameters that cannot be deterministically and uniquely evaluated from topographic, climatic, physical, and chemical characteristics of the watershed and compounds of interest. Calibration would be based on a simulation to evaluate parameters under a variety of climatic conditions. The calibration procedure results in parameter values that produce the best overall agreement between simulated and observed values (e.g., flow, concentrations, loads) throughout the calibration period. Validation is an independent assessment of the parameter values, using a separate time period at the same location or separate monitoring locations. After model calibration and validation, sensitivity analysis can be conducted to evaluate model response to selected parameters. In some cases, sensitivity analysis can provide important insight into whether a gap that existed was important or not for describing the system.

A key goal of the watershed model is to provide a tool that can provide estimates of pollutant loads for different land areas. This can be accomplished by constructing the model using a hydrologic response unit (HRU) basis, where each HRU typically represents the intersection of land use / land cover, soil characteristics, slope, weather station assignment, and other characteristics if necessary. To ensure correct jurisdictional or other boundary (e.g., MS4) representation, HRUs can also be distinguished by political boundaries. HRUs are simulated on a unit-area basis. If constructed properly, the system will then allow for a ready accounting of source loads generated by select spatial units by tabulating the individual HRU responses. Source parameters can be varied by individual HRUs and by specific HRUs within a given geographic area to account for site-specific information on pollutant loading.

3.2.1 Previous HRU Development

The King County HSPF models for the Green/Duwamish watershed are built on a consistent basis, developed by AQUA TERRA (AQUA TERRA and King County, 2003; King County, 2013a). King Co. (2013a) describes development of a comprehensive set of models for the WRIA 9 area, including both the Green/Duwamish watershed and areas draining direct to Puget Sound. The portions of the Green/Duwamish watershed within the City of Seattle are not included.

The upland portions of the watersheds are simulated using HRUs that consist of an overlay of land use, geology, and slope. These categories are optimized for hydrologic simulation in the coastal Pacific Northwest, reflecting the combined effects of volcanism and Quaternary glaciers. Surface geology is separated into four categories that reflect their hydrologic response:

1. till (the glacial till that is generally present on uplands along the river valleys),
2. outwash (the valley fill created by the melting of the glaciers),
3. saturated soils (soils with high water table primarily located along river corridors), and
4. bedrock (areas with shallow soils over relatively impervious bedrock).

The soils/geology classification is further subdivided into slope categories for all except the relatively flat outwash and saturated soils categories. The remainder are divided into flat (0-5%), low slope (5-10%), medium (10-15%), and steep (>15%) categories. Different hydrologic parameters are assigned to different combinations of soils and slope.

On top of the soils/slope characterization, HRUs are separated based on land use/cover. The following general categories were initially assigned:

1. forest,
2. pasture/agricultural,
3. cropland,
4. forest residential,
5. low density residential,
6. high density residential, and
7. commercial/industrial.

Connected impervious land areas were separated from the overall land cover distribution based on generalized percentages of effective (i.e., directly connected) impervious area. After the initial analysis, the impervious area in major roads was segregated as a separate category of impervious land.

Each tributary drainage is represented in a separate model. All models are calibrated, to varying degrees, to hydrology. King County has also endeavored to develop contaminant transport models for suspended sediment, nutrients, and copper – although water quality calibration has not been completed in many of the tributary subwatersheds. AQUA TERRA calibrated the models to TSS, copper, and DO/BOD in several of the models based in King County (2003).

Hydrologic calibration has been conducted at varying degrees for different tributaries, depending on whether local calibration gages are available versus using generalized parameters for the local ecoregion. In general, hydrologic calibration appears acceptable. Water quality calibration has been attempted for some of the tributary subwatersheds, but appears to be ongoing.

King County (2013a) describes updating, calibration and testing of HSPF models for use in this study the WRIA 9 project that use SUSTAIN's modeling for stormwater retrofit analysis. Inputs to SUSTAIN included hourly HSPF model outputs from October 1948 through September 2009 for flow and total suspended solids (TSS). According to this documentation, 8 of 17 basins for the WRIA 9 study had been calibrated for TSS. Calibration quality

ranged from poor (Black River and Covington Creek) to excellent (Big Soos Creek) for TSS. Note that the study area included drainage areas in addition to those in the Green/Duwamish River Watershed.

The 2013 report further describes the basis of HRU development. Land use and land cover is based on 30-m resolution 2007 satellite-derived dataset with 14 land use categories from the University of Washington. Two tables from the King County report are reproduced below (Table 17 and Table 18). These define the modeled land use/cover categories and model HRU descriptions.

Table 17. Land cover categories used in the development of the HSPF model.

Land Use	Description	Land Cover
Heavy Urban	Commercial / industrial with lawns, rooftops, pavement, roads	High grass and Impervious surfaces
Medium Urban	Medium to high density residential with lawns, rooftops, pavement, roads	Medium grass and Impervious surfaces
Light Urban	Low density residential with lawns, rooftops, pavement, roads	Low grass and Impervious surfaces
Cleared for Development	Compacted lands cleared for development	Cleared Lands
Grass, Grasslands	Lawns, parks, meadows, golf courses, etc. with some roads	Grass
Deciduous and Mixed Forest	Forested lands with some roads	Forest
Coniferous Forest	Forest lands with some roads	Forest
Clear cut Forest	Recently cleared forested lands with some roads	Clear cut
Regenerating Forest	Early stages of tree growth with some roads	Regenerating Forest
Agriculture	Agriculture lands used for animal or crops with some roads	Agricultures
Non-forested wetlands	Visible wetlands with some roads	Wetlands
Open Water	Open water	Open Water
Snow, Bare rock	Higher elevations, dominated by snow cover and/or bare rock with some roads. For this study the amount of areas are inconsequential and are reassigned to keep permutations to a minimum.	Modeled as medium grass and Impervious surfaces
Shorelines	Slivers of landscape buffering larger receiving bodies of water with some roads	Modeled as grass

Land Use	Description	Land Cover
Roads	External dataset applied	Road impervious surface and grass
Added wetlands	Added wetlands using alternative data source	Wetlands

Table 18. HRU numbering scheme from King County (2013b) with associated surficial geology, land cover, slope

HRU Number	Surficial Geology	Land Cover	Slope	Description	Short Descr.
1	Till	Roads grass	Flat	Till Road Grass Flat	TR1
3			Moderate	Till Road Grass MED	TR3
11		Commercial grass	Flat	Till Road Grass Flat	TC1
13			Moderate	Till Road Grass MED	TC3
21		High Density Residential grass	Flat	Till Road Grass Flat	THR1
23			Moderate	Till Road Grass MED	THR3
31		Low Density Residential grass	Flat	Till Road Grass Flat	TLR1
33			Moderate	Till Road Grass MED	TLR3
41		Cleared Lands	Flat	Till Road Grass Flat	TCLR1
43			Moderate	Till Road Grass MED	TCLR3
51		Grasslands	Flat	Till Road Grass Flat	TGR1
53			Moderate	Till Road Grass MED	TGR3
61		Forest	Flat	Till Road Grass Flat	TF1
63			Moderate	Till Road Grass MED	TF3
71		Clear Cuts	Flat	Till Road Grass Flat	TCC1
73			Moderate	Till Road Grass MED	TCC3
81		Forest Regeneration	Flat	Till Road Grass Flat	TFRG1
83			Moderate	Till Road Grass MED	TFRG3
91		Agriculture	Flat	Till Road Grass Flat	TAG1
93			Moderate	Till Road Grass MED	TAG3
100	Outwash	Roads grass	N/A	OUTWASH, Road Grass	OR
101		Commercial grass		OUTWASH, COM Grass	OC
102		High Density		OUTWASH, HD Grass	OHD

HRU Number	Surficial Geology	Land Cover	Slope	Description	Short Descr.
		Residential grass			
103		Low Density Residential grass		OUTWASH, LD Grass	OLD
104		Cleared Lands		OUTWASH, Cleared	OCLR
105		Grasslands		OUTWASH, Grassland	OGR
106		Forest		OUTWASH, Forest	OF
107		Clear Cuts		OUTWASH, Clear Cut	OCC
108		Forest Regeneration		OUTWASH, Forest Regen	OFRG
109		Agriculture		OUTWASH, Agriculture	OAGR
110	Saturated	Roads grass		SATURATED, Road grass	SRds
111		Commercial grass		SATURATED, Com grass	SC
112		High Density Residential grass		SATURATED, HD Grass	SHR
113		Low Density Residential grass		SATURATED, LD Grass	SLR
114		Cleared Lands		SATURATED, Cleared	SCLR
115		Grasslands		SATURATED, Grass	SGR
116		Forest		SATURATED, Forest	SF
117		Clear Cuts		SATURATED, Clear Cut	SCC
118		Forest Regeneration		SATURATED, Forest Reg	SFRG
119		Agriculture		SATURATED, Agriculture	SAGR
120		Wetlands		SATURATED, Wetland	WET
150	Impervious	LD Residential		EIA Low Den Residential	L-EIA
151		HD Residential		EIA High Den Residential	H-EIA
152		Commercial		EUA Commercial	C-EIA
153		Roads		EIA Roads	R-EIA

3.2.2 Land-Based Pollutant Representation

Loading processes for pollutants in LSPC will be represented for each land unit (HRU) using the PQUAL modules (simulation of pollutants for pervious land segments) and IQUAL (simulation of quality constituents for impervious land segments) modules, which are also identical to those in HSPF. These modules allow for the simulation of pollutant loading as solids/sediment-associated, as a buildup-washoff relationship, as an event mean concentration in land segment outflow, or a combination of the three.

For the purposes of developing watershed loading models of contaminants of concern in the Duwamish PLA (PCBs, PAHs, dioxins, arsenic, and several metals), the King County models provide a strong hydrologic foundation at the large watershed scale. One limitation is that these models do not model the combined sewer area and separate storm sewer urban drainages near the LDW. There is also limited capacity to specify different loading rates from specific parcels without additional refinement of the models. It appears that the King County models can be directly built upon to address loading from rural areas with diffuse sources. In the urban areas it will likely be necessary to refine the models to distinguish certain source areas as specific upland pervious and impervious HRUs. It may also be necessary to retabulate urban HRUs on the basis of whether they are served by combined or separate storm sewers and to reflect specific information on upland sites.

These modifications would likely not require any major changes to the hydrologic calibration of the HSPF models. Hydrologic representation refers to the LSPC modules or algorithms used to simulate hydrologic processes (e.g., surface runoff, ET, and infiltration). The LSPC PWATER (water budget simulation for pervious land segments) and IWATER (water budget simulation for impervious land segments) modules, which are identical to those in HSPF, will be used to represent hydrology for all pervious and impervious land units (Bicknell et al., 2001). During hydrology calibration, land segment hydrology parameters are adjusted iteratively to achieve agreement between simulated and observed stream flows at specified locations throughout the basin.

Source areas, such as specific urban industrial areas, could be separated into specific HRU categories that inherit the hydrologic parameters of their parent HRU, but have different pollutant loading characteristics. This may be informed, in part, by source area investigations conducted for the LDW. For instance, areas known to be sources of PCBs and connected to the LDW by separate stormwater drainages could have their own pollutant characteristics. Doing this in an efficient manner is contingent on access the spatial coverages or processing spreadsheets that have been used to develop the existing King County models. Pollutants

For the Green-Duwamish watershed, and given the focus on PCBs, cPAHs, 2,3,7,8 TCDD, arsenic, DEHP, copper, zinc, and mercury, buildup/washoff (with atmospheric deposition) is most likely the best choice for impervious land segment simulation of pollutant generation. For pervious land, potency (e.g., pounds of the COC per ton of sediment eroded) plus specification of concentrations in subsurface flow pathways, is proposed. A buildup/washoff component on pervious land can also be included in addition to potency if atmospheric deposition onto saturated surfaces is a particular concern.

When using the buildup-washoff method, pollutants, including indirect atmospheric deposition, are modeled as accumulating and then washing off based on rainfall and overland flow. Accumulation rates are assigned to HRUs to simulate buildup of pollutants on the land surface, along with an asymptotic maximum storage. Accumulation rates can be estimated on the basis of typical pollutant production rates for sources associated with different HRU types. Both local data and literature will inform these rates. These values serve as starting points for water quality calibration.

During calibration for chemical parameters, the first step is to assign groundwater concentrations to pervious land segments based on available data and literature. The next step is to verify assign initial build up washoff and/or potency and modify iteratively to verify that unit area loading rates were reasonable compared to literature values or local land use loading information. After ensuring reasonable upland loading rates, calibration to instream observations will be carried out to refine the simulation.

3.2.3 Instream Water Quality Calibration

Although the focus of the modeling effort is on toxic parameters, movement of sediment must also be represented correctly to ensure proper simulation of loads (discussed further below). Unlike flow, continuous measurement of water quality is not available at any monitoring station in the watershed (except for continuous USGS monitoring at 12113390 started in 2013, which includes flow and turbidity). The calibration to instream

concentration must therefore rely on comparison of continuous model output to point-in-time-and-space observations.

In this project, a two-stage approach will be used for water quality calibration to instream measures. In the first stage, the model calibration will be guided by a visual comparison approach aimed at reproducing the observed trend and overall dynamics of the system. After the model has been calibrated to the trend and overall dynamics, the second stage involves fine tuning the parameters and then calculating various error statistics to find the most appropriate calibration within the range of state spaces found in stage one.

3.2.3.1 Sediment (Channel)

Sediment (bedded and suspended) is one of the more challenging water quality parameters to simulate with watershed models because observed instream TSS or SSC concentrations depend on the net effects of a variety of upland and stream reach processes. The LSPC/HSPF modules used to represent sediment include SEDMNT (pervious land production and removal of sediment), SOLIDS (accumulation and removal of solids on impervious land), and SEDTRN (transport and behavior of inorganic sediment in streams including scour and deposition). During calibration sediment parameters are adjusted in accordance with guidelines established in EPA BASINS Technical Note 8: *Sediment Parameters and Calibration guidance to HSP*F (USEPA, 2006) and *Sediment Calibration Procedures and Guidelines for Watershed Modeling* (Donigian and Love, 2003). Sediment and solids calibration should use a weight of evidence approach. The first step in calibration involved setting channel erosion to values that achieve a reasonable fit to observations when upland erosion is held to reasonable values consistent with the literature and soil survey data. Second, the long-term behavior of sediment in channels was constrained to a reasonable representation in which degradation or aggradation amounts are physically realistic and consistent with available local information. Finally, results from detailed local stream studies will be used to further ensure that the model provides a reasonable representation in specific areas.

3.2.4 Point Sources

The majority of NPDES permits in the study area are general permits for stormwater (municipal, industrial and construction) and specific industrial processes (such as Sand & Gravel and Boatyards), which are proposed to be incorporated as upland, runoff-based processes in the LSPC watershed model and not included in the model as an explicit time series input of direct discharge to a receiving stream. There are five individual permits in the Lower Duwamish and Lower Green watersheds; however, it is likely that most of these will not be included explicitly in the model due to size, nature of the "discharge," type of facility, and/or the ability to also be represented as an upland inputs. Additional comments on point sources are provided near the end of this memo. Note that this section does not cover CSOs since treatment of these was discussed in a previous section.

3.2.5 Status of Calibration of Existing Models

The WRIA 9 models have been calibrated for flow and sediment, as reported in King Co. (2013a). Additional refinements of the flow and sediment calibration may be needed; however, the report on existing models gives an indication of the degree of calibration that is likely to be achieved. The area covered in the WRIA 9 models that drains to the LDW constitutes 20 linked HSPF models. Half (10) of these models do not have calibration data. For the other 10 (excluding the WRIA models that drain directly to Puget Sound) the quality of hydrologic calibration is generally rated as "good." In contrast, the suspended solids calibration ratings range from "poor" (Black River and Covington) to "excellent" (Big Soos). It is evident that additional effort may be needed on the suspended solids calibration because the transport of most of the constituents of concern depends in large part on the movement of sediment.

3.3 WATERSHED WATER QUALITY DATA

The next sections summarize the data and information available for calibration of the watershed model for water quality. The information described will be used to describe pollutant sources in the modeling environment and provide the basis for instream calibration. Significant gaps and strategies can then be identified within this context.

3.3.1 RI and FS - Watershed Components

As summarized earlier, the RI reports on data collected through October 2006 and available as of 2008. The FS supplements the RI dataset by adding samples collected through April 2010. The following discussion presents information relative to watershed-based sources.

Section 9 of the RI summarizes potential ongoing sources that could lead to sediment recontamination following cleanup of the LDW. Three primary watershed-based sources are atmospheric deposition, upstream surface water inputs from the Green River, direct discharges to the LDW including CSOs and storm drains, ground water, and bank erosion in the LDW. Each of these potential source categories is analyzed in detail, providing important information on the state of knowledge and data as of 2007 in the RI.

1. Atmospheric deposition was characterized based on a number of studies, most notably the two phases of King County data collection.
2. Upstream surface water inputs from the Green River were relatively poorly constrained.
3. Direct discharges to the LDW include both CSOs (with emergency overflows) and both public and private separate storm sewer discharges (the latter are about 24% and 15% of the drainage area, respectively, according to FS). Residual sources within the storm sewer and combined sewer drainage are extremely heterogeneous and only incompletely characterized (as of 2007), creating a challenge for modeling chemical loads from these sources.

Data gaps based on the RI/FS relative the watershed were large. These included instream data to define watershed inputs from the Green River as well as limited atmospheric deposition data. Many of these gaps have been filled, or have started to be filled by more recent studies. These are discussed further below.

3.3.2 EIM Database

In the previous data and model evaluation memo, data available from the 1990's through 2012 were summarized for the watershed indicating modest amounts of water column data for TSS, copper, mercury, zinc, PAHs, and PCBs. There appeared to be no earlier 2,3,7,8-TCDD or DEHP for the water column in the watershed, at least based on the previous compilation effort. Surface sediment-associated samples were more prevalent. Much of the more recent data collection by King County, USGS, and others were not included in this earlier compilation for the PLA, and this was also the case for a recent data compilation by Leidos (2014) for Ecology.

Tetra Tech downloaded an updated dataset from the EIM database in April 2015. Data from January 2000 through April 2015 were summarized for the PLA priority pollutants. Results from various ongoing data collection efforts are still not included in this database pull. Data within the Lower, Middle, and Upper watershed (as defined in previous documents) suggest the following:

- Water Column
    - In the Lower watershed, total and dissolved metals or metalloids from 2001 through 2012 counts (station x # of samples) ranged from 39 to 76 for total and 41 to 151 for dissolved metals. In the Middle watershed, counts ranged 65 to 139 for total and 73 to141 for dissolved metals (data were from 2000-2015). Some limited total recoverable metal analyses were also available.
    - cPAHs (based on the seven individual, prioritized PLA parameters) included 20 sample counts from 2008-2012 in the Lower watershed. There were fewer data in the Middle watershed.

  - PCB data, grouped into homologs, ranged from 23 to 667 counts from 2005-2008 in the Lower watershed. None were found in the Middle watershed.
  - No water column data was located in the Upper watershed.
- Surface Sediment
  - There were some metals data in the Lower and Middle watershed (2000-2010). Total recoverable samples ranged from 15 counts in the Lower and 31-37 in the Middle watershed.
  - PAHs had similar count ranges as metals.
  - No new PCB data was located in the EIM database.
  - Single digit sediment samples were found for the Upper watershed.
- No 2,3,7,8 TCDD or BEHP data were located either in the water column (ambient) or sediment.
- EIM data since 2010 suggested few new surface water data collected in the watershed were uploaded to this database. There were less than 10 samples from 2012 and 2015 for cPAHs, dissolved arsenic, dissolved and total copper, dissolved and total zinc, and total arsenic. However, recent presentations indicate that additional data collection is ongoing.

3.3.3 Recent Data and Studies

A number of data collection efforts have been conducted (or are ongoing) in an effort to fill data gaps in the watershed since the RI/FS, which covered data collected through early 2010. These collection efforts are essential to development of the PLA watershed model.

3.3.3.1 Ecology

Ecology is leading source control efforts for the LDW in cooperation with the City of Seattle, King County, and USEPA. Source control is the "process of working to find and control releases of pollution to waterway sediments to prepare for cleanup and prevent sediment recontamination." As part of this effort, a report entitled, A *Compendium of Existing Environmental Information*, was prepared for Ecology to aid in understanding of existing conditions and sources of pollutants in the watershed upstream of the LDW (Leidos, 2014). The stated objectives of the report were:

- Provide an overview of the Green-Duwamish River watershed upstream of the LDW Site (Section 1 and Section 2).
- Summarize relevant studies that have been performed to characterize sediments and surface water in the Green-Duwamish River and its tributaries (Section 3).
- Compile and map chemical data available as of February 2014 for sediment, suspended solids, and whole water upstream of the LDW Site (Section 4).
- Identify and map locations of potential sources of LDW COCs to the Green-Duwamish River, including contaminated sites, facilities with National Pollutant Discharge Elimination System (NPDES) permits, fully-regulated hazardous waste generators, and facilities registered with the Puget Sound Clean Air Agency (Section 5).
- Identify data gaps and provide recommendations for further source control activities (Section 6).

Also as part of the effort, Leidos collected and compiled municipal stormwater system maps for each of the jurisdictions in the Green-Duwamish River watershed.

In Section 3, the report summarizes the following studies, considered most relevant.

1. Duwamish River Sediment Sampling and Analysis (Ecology)
2. Green River Suspended Sediment Contaminant Loading Study (Ecology)
3. Stream Sediment Monitoring in the Green River Basin (King County)
4. Green River Study: Surface Water (King County)
5. Green River Study: Suspended Solids Characterization (King County)

6. Assessing Sediment and Toxic Chemical Loads from the Green River to the Lower Duwamish Waterway (USGS)
7. Screening Investigation of Creeks in Mining Districts (Ecology)
8. Green Duwamish Water Quality Data Report, Year 2003 (King County)
9. Screening-Level Risk Assessment of the Green River Watershed (King County)
10. Water Quality Statistical and Pollutant Loadings Analysis (King County)
11. Bulk Atmospheric Air Deposition Study (King County)
12. Air Deposition Scoping Study (Ecology)

The data from most of these studies are discussed further in a separate section below. The report indicates that additional studies that were reviewed (and provided in an Appendix) but were not considered directly relevant including water quality studies not related to the COCs, TMDL assessments, habitat restoration, and flow management and flood control.

In Section 4 and associated appendices of Leidos (2014), chemical data for sediment and surface water primarily from Ecology's EIM database were summarized. The report notes that only samples with chemical data were included. Summary statistics and maps of select analytes (arsenic, cadmium, zinc, total PCBs, dioxin/furans, total cPAHs) were presented. Surface water sampling data available at the time this dataset was compiled included only arsenic with a small number of samples were available from the Black River and Middle Green River study units. A greater amount of surface sediment data was compiled and summarized.

In Section 5, facilities or sites that may represent potential contaminant sources to were identified using Ecology's Facility/Site, Integrated Site Information System (ISIS) and Water Quality Permitting and Reporting Information System (PARIS) databases, and Puget Sound Clean Air Agency (PSCAA) registration lists for the 28 zip codes within WRIA 9. The process led to identification of 1,027 sites for additional evaluation. Of these, about half were considered most important and included contaminated sites, sites with active discharge permits, and sites that are active hazardous waste generators.

Summary of Data Gaps

The Leidos (2014) report provided a summary of data gaps for the watershed data. The summary covered data gaps and recommendations for digital mapping, sediment and surface water characterization, and identification of potential sources. Information on the latter two is provided below.

The sediment and surface water datasets compiled and summarized for the project were based primarily on data available in Ecology's EIM, with the exception of recent King County surface sediment data. Leidos (2014) indicates that the surface sediment dataset developed for the report was believed to be reasonably complete. Most of the available sediment data is over 10 years old but the recent data collection by King County are important supplements. The report further suggests that the surface water dataset compile was not complete. Additional sources of surface water data, including King County's most recent sampling effort, needed to be identified/incorporated in follow up work. The report concluded that there were insufficient data to link elevated concentrations in sediment with potential contaminant sources.

The report concludes that concentrations of COCs and affected environmental media are needed for many identified sites. Some of the recommendations put forth included the following:

- Conduct additional data mining of the EIM System database in order to refine the list of sites that require further review.
- Gather information on unregulated stormwater outfalls.
- Gather information regarding the discharge locations of the 143 sites with active discharge permits to determine the potential for sediment contamination associated with these discharges.
- Confirm MS4 maps or outfall locations. Not all areas within a municipality contribute runoff to the Green River or its tributaries, such as areas that infiltrate stormwater to the ground.

- Additional information is needed before conclusions can be made regarding area loading rates for particular contaminants entrained in stormwater discharges.
- Confirm hazardous waste generator status (LQG, MQG, etc.) for 107 sites with active hazardous waste generator numbers.
- Additional review of the NOVs issued to PSCAA-registered facilities is suggested to determine the nature of the NOV and if there is potential for release of sediment COCs from these sites from air deposition.

3.3.3.2 USGS

USGS Green River Duwamish Chemical Loading Study

The USGS monitoring effort underway and conducting via an agreement with Ecology was discussed in Conn and Black (2014). In addition, USGS presented initial results on sediment and chemical loading from the Green-Duwamish River watershed to the LDW at a March 19, 2015 meeting of the TAC. Results have not been published as of the writing of this memo. This supplements sediment loading data previously collected by Ecology (2009).

The effort is focused on continuous data collection at USGS 12113390 - Duwamish River at Golf Course at Tukwila, WA (RM 10.8), and discrete sampling at the same location which is located above the LDW. Continuous gaging began in November 2013 with collection for discharge, turbidity, velocity, height, and temperature (note: a second station is also being installed). The discrete sampling at the site began in 2013 (and scheduled to continue through June 2015) and has included thus far approximately 25 samples of whole water and suspended sediment over a range of flow and turbidity conditions. Measurements were made for SSC, particle size distribution (PSD), and water quality parameters (pH, temp, DO, specific conductance). Eight bed sediment samples were taken and tested for 209 PCB congeners, dioxins/furans, 2,3,7,8 TCDD, metals (total and dissolved, including the PLA metals of interest), PAHs, DEHP, other SVOCS, VOCs, pesticides, butyl tins, hexavalent chromium, and TOC/DOC. USGS developed a curve to estimate sediment from the continuous turbidity measurements being taken at the continuous station. USGS is also developing annual loading estimates for sediment and chemicals. Publication of data and loading estimates is expected to occur during summer 2015.

In sampling thus far, frequently detected pollutants included metals, PCB congeners, and TOC in both water and sediment. Dioxins/furans and PAHs were frequently detected in sediment, and occasionally detected in water. Also occasionally detected were DEHP, diethyl phthalate, benzyl alcohol, benzoic acid, 4-methylphenol (in water and sediment). Butyl tins were occasionally detected in sediment. All others were not detected.

Pending funding, a phase 3 would continue from fall 2015 through spring 2017 and include additional continuous monitoring and discrete sampling at one or more locations in Green/Duwamish watershed, as well as improved sediment and chemical loading estimates based on source characterization.

3.3.3.3 King County

Sediment Quality in the Green River Watershed

King County's report, *Sediment Quality in the Green River Watershed* (King County, 2014) described an assessment of sediment quality in the watershed to characterize chemical concentrations and to better understand the relative differences of sediment quality between tributary basins and the Green River. Parameters included metals (incl. mercury), PAHs PCB (as Aroclors), dioxin/furan, phthalates, and others. Four basins were sampled in 2012, and 3 in 2008-2010. There was one sample per site. Note that metals are reported simultaneously as extractable metals and total metals. Table 19 shows the frequency of detection for the PLA prioritized parameters. Figure 12 provides the sampling locations.

Table 19. Frequency of detection for parameters in King County sediment sampling (2008-2012)

Parameter	Frequency of Detection
Arsenic	58/58
Copper	58/58
Zinc	58/58
Mercury	58/58
PCBs (as Aroclors)	19/58
Benzo(a)anthracene	33/58
Benzo(a)pyrene	34/58
Benzo(b)fluoranthene	18/26
Benzo(k)fluoranthene	16/26
Chrysene	40/58
Dibenzo(a,h)anthracene	10/58
Indeno(1,2,3-Cd)Pyrene	20/58
DEHP	51/58
Dioxin TEQ*, **	7/7

* Dioxin and furan congener data were converted to toxicity equivalents (TEQs) because TEQs provide a toxicity‐based approach to interpreting the dioxin and furan congener data. Dioxin and furan congener concentrations were converted to TEQs based on 2,3,7,8 TCDD toxicity by multiplying the concentration of an individual congener by its toxicity equivalent factor (TEF) for mammals from Van den Berg et al. (2006) to result in a TEQ concentration. The total dioxin TEQ was based on summing the 17 TEQ values. Whenever a dioxin or furan was not detected, the TEF was applied to the full non‐detect value (or U qualified value).

** All the samples were collected in 2012. The stations were typically located near mouths of streams (two different Mill Creeks, Soos, Newaukum, and Springbrook); the most upstream and downstream stations on Green River were also sampled.

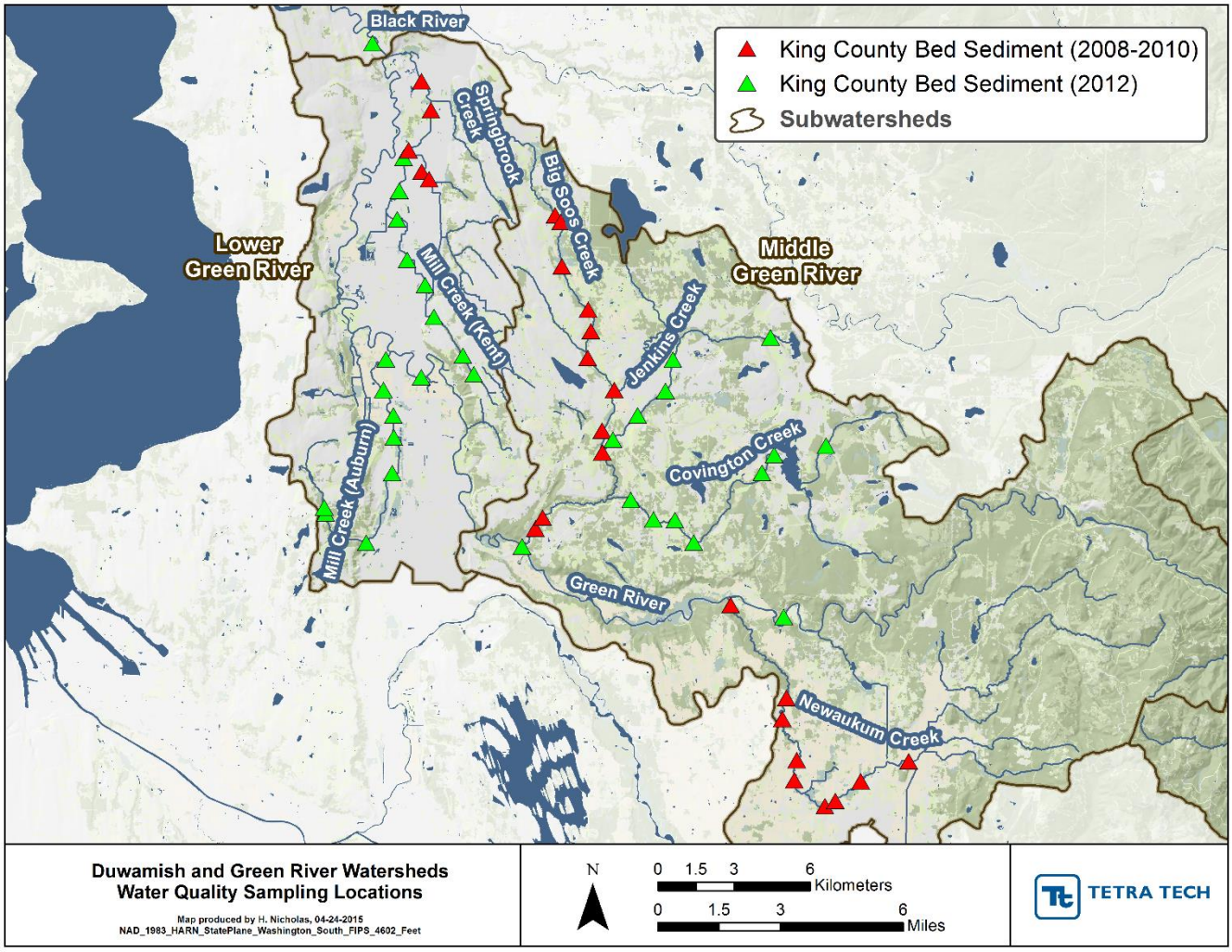

Figure 12. King County bed sediment sampling (2008-2012)

Surface Water

King County describes recent surface water sampling in two reports (King County 2014b and 2015). The effort included collection of arsenic, PAHs and PCBs (as congeners) in 2011 and 2012 at four major tributaries and two main stem stations. The second report describes upper and middle Green River watershed data including TSS, arsenic, PAHs and PCBs (as congeners) in samples collected in 2013 and 2014 at 3 stations - two above Howard Hanson Dam; and one below Dam. The data include both baseflow and storm event sampling. Table 20 shows the frequency of detection. Flow was also collected during sampling.

Table 20. Frequency of detection for parameters in King County surface water sampling (2011-2014)

Station	Dates	TSS	PCBs*	cPAHs**	Arsenic	
					Total	Dissolved
KP319	2013-2014	10/10	6/6	1/10 to 4/10	6/6	6/6

Station	Dates	TSS	PCBs*	cPAHs**	Arsenic	
					Total	Dissolved
SC319	2013	2/6	6/6	0/6 to 1/6***	2/6	1/6
UG319	2013	2/6	8/8	0/6 all	10/10	10/10
FG319	2011-2012	9/9	9/9	0/9 to 2/9	9/9	9/9
322	2011-2012	9/9	9/9	0/9 to 4/9	9/9	9/9
A320	2011-2012	9/9	9/9	0/9 to 6/9	9/9	9/9
A315	2011-2012	9/9	9/9	1/9 to 8/9	9/9	9/9
PS317	2011-2012	9/9	9/9	6/9 to 9/9	9/9	9/9
FL319	2011-2012	9/9	9/9	1/9 to 7/9	9/9	9/9

* Sum of 209 congeners

** All seven Tt cPAHs were monitored.

*** Benzo(b,j,k)-fluoranthene was detected once; all other samples were nondetects.

Suspended Sediment Study

King County is also conducting suspended sediment (sediment traps and filtered solids) sampling in the Green River and select tributaries. The report is not yet published, and the following summary is derived from Leidos (2014), a presentation by King County to the TAC in spring 2015, and a previous sampling plan (King County, 2013c). The study is using station locations from 2011-2012 surface water study. Two sampling methods are employed: sediment traps, and filtered samples. Sediment trap sampling occurs over a period of three to four months. Samples were collected Q4 2012 through Q4 2014. All prioritized parameters are being analyzed. PCBs are as Aroclors. Table 21 shows number sampling events (header row; in parentheses) reported in Leidos (2014). A map showing suspended sediment stations along with those for surface water for King County are shown in Figure 13 below (note: the USGS station is added for reference).

Table 21. Frequency of detection for parameters in King County suspended sediment sampling (2013-2014)

Station	Sediment Traps (4)	Filtered Baseflow (1)	Filtered Storm Event (5)
FG319	X	X	X
322	X	X	X
A320	X	X	X
A315*	X	X	X
PS317**		X	X
FL319	X	X	X

* Mill Creek will have two sediment traps of different designs placed simultaneously

** Black River will have only three filtered storm event samples

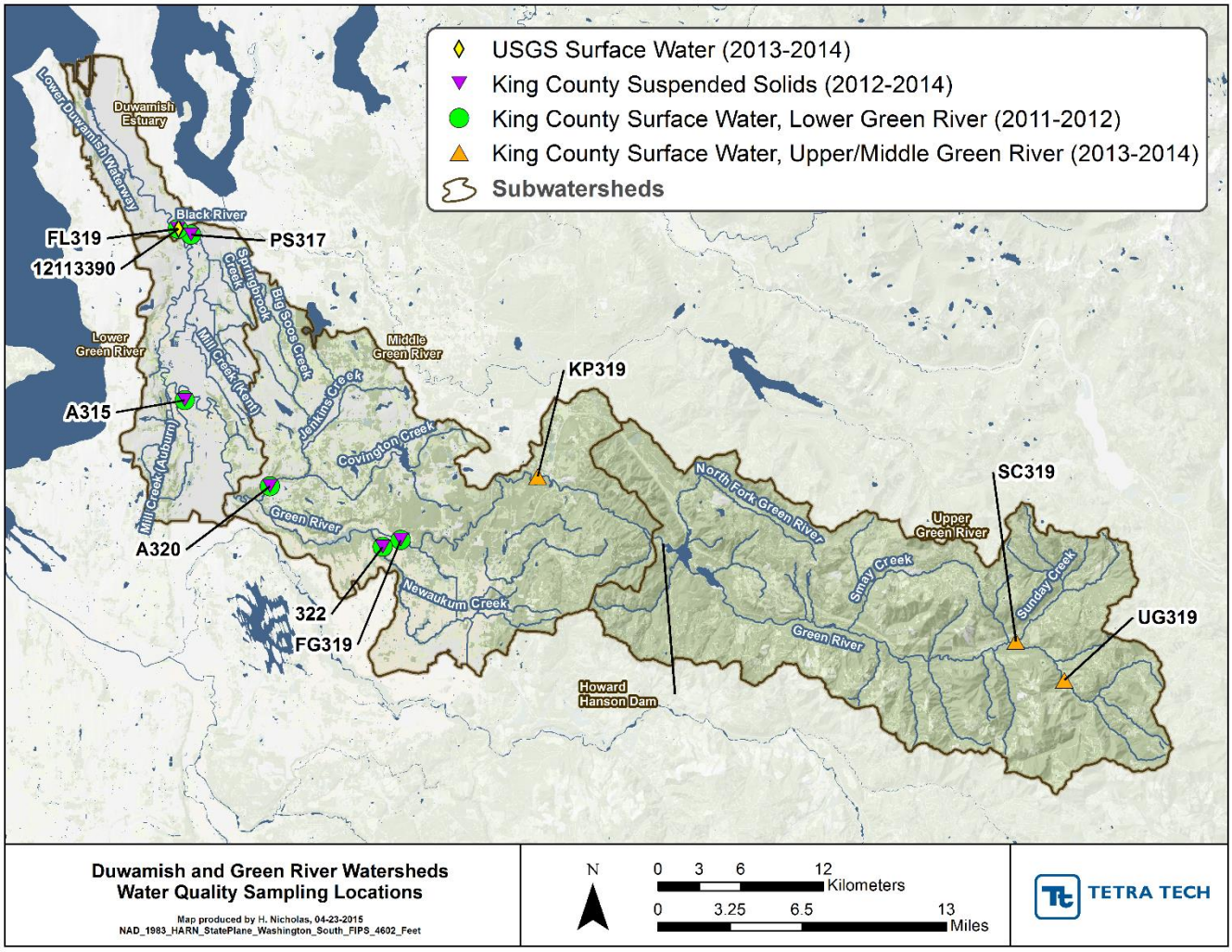

Figure 13. Suspended solids and surface water sampling by King County and USGS (2011-2014)

3.3.4 Additional Studies

In addition to the more recent sources of instream water quality data, earlier work by Ecology and King County may be needed to help validate the model (calibration is likely to be focused on the more recent data).

3.3.4.1 Green-Duwamish Screening Level Assessment

An earlier King County effort that compiled data from a number of sources was the screening-level risk assessment (SLRA) for Green-Duwamish watershed, as part of the Green-Duwamish Water Quality Assessment (WQA). The SLRA was based on surface water quality data. Data collected between 1999 and 2003 were used in the SLRA; sources of data included King County, Ecology, and USGS.

3.3.4.2 USGS National Water Quality Assessment (1994-2003)

The USGS National Water Quality Assessment (1994-2003) describes an effort where USGS collected water samples monthly between March 1996 and April 1998, with additional sampling during storm runoff and high-flow events. Suspended sediment samples were collected 24 to 42 times per selected subwatershed during this period. USGS calculated loads based on these samples. Field measurements and laboratory analyses were collected by USGS from these locations:

1. Duwamish River at Golf Course at Tukwila; drainage area 461 square miles; integrated land use (urban, mixed agriculture, forestry practices).
2. Springbrook Creek at Tukwila; drainage area 20 square miles; indicator for urban land use (commercial, light industry, residential).
3. Big Soos Creek above Hatchery near Auburn; drainage area 66.7 square miles; indicator for suburban/urban land use.
4. Newaukum Creek near Black Diamond; drainage area 27.4 square miles; indicator for agricultural land use (hobby farms, dairy).
5. Green River above Twin Camp Creek near Lester; drainage area 16.5 square miles; indicator for forestry practices land use.

3.3.4.3 Green River Suspended Sediment Contaminant Loading Study (Ecology)

Ecology conducted a study on contaminant loading to the LDW from suspended sediment in the Green River in 2008-2009. Samples of suspended sediment were collected during seven sampling events (over a wide range of flow conditions) at the 199th Street footbridge in Tukwila, approximately 1.8 miles upstream of the LDW boundary (Ecology, 2009). The sediments collected were analyzed for total suspended solids (TSS), total organic carbon (TOC), PCBs, dioxins/furans, cPAHs, and arsenic.

3.3.4.4 USACE Dredging

The Upper Turning Basin is frequently dredged and sediment quality there is based on core data collected by USACE for dredged material characterization. These cores likely provide an integrative measure of upstream sources over time. If new dredging has occurred recently, results from these can be used to support calibration and validation of the watershed model.

3.3.4.5 Land-Use Based Loading

Local data can be used to parameterize and calibrate land-use based loading. The following sections summarize the data available to constrain this aspect of the watershed model, and to support the framework to distinguish the variable pollutant-generating character of land-based activities and covers.

Herrera (2003, 2005, and 2007)

Herrera Environmental Consultants (2004, 2005) provide summaries of water quality data collected in the Green-Duwamish watershed during 2001 – 2003 (also discussed in King County, 2005?) All of the recommended parameters were included, with the exception of 2,3,7,8 TCDD. Data were analyzed from 18 stations, eight of which were located on major streams, and ten of which were downstream of small drainage areas (0.5 to 3.9 mi^2) of fairly homogenous land uses. The sites were characterized as representing forest (2), agriculture, (2), low/medium density development (4), and high density development (2). Box and whisker concentration plots are shown for the metals, separately for baseflow and storm events for each of the sites. DEHP and cPAHs were summarized more qualitatively, and summary statistics and graphs were not presented in the main report. PCBs (as Aroclors) were not detected in any of the samples at the reported quantification limit of 0.04 to 0.06 μg/L.

These studies have utility for estimating metals concentrations by visual interpretation from the box plots, but interpretation of organics is not possible without the source data or additional documentation.

Herrera Environmental Consultants (2007) provides a detailed statistical analysis of the water quality data summarized in the two previously cited reports. The focus is primarily conventional water quality parameters, but total and dissolved copper, zinc, and mercury are included (note that arsenic is excluded). Several types of analysis were explored in detail, including comparison of sampling approaches, storm flow versus baseflow, correlations between parameters, as well as correlations between each parameter and hydrology measures, a principle component analysis, a loading rate analysis, and a correlation analysis of loading rates to land uses. The study is useful for providing baseflow concentrations, storm event concentration ranges, and loading rates by land use type. For the developed uses, estimation of model parameters would be better served by examining relationships to impervious area and road density rather than the density classes used by the report. Even so, there appears to be considerably variability in the concentrations and loading rates not explained by development density.

Puget Sound Toxics Studies

Studies relating toxic pollutants to land uses have been conducted elsewhere in the region. As part of Phase 3 of the Puget Sound Toxics Loading Analysis, Herrera Environmental Consultants (2011) analyzed monitoring data from multiple small drainage areas representative of specific land uses collected from 2009 – 2010 in the Puyallup and Snohomish watersheds. This study is similar in design to those conducted in the Green-Duwamish watershed described above. Sixteen sites were selected with drainage areas ranging from 0.3 to 6.4 mi^2, eight each in the Puyallup and Snohomish watersheds. Within each watershed, two sites were chosen to represent each of the following land uses: forest, agriculture, residential, and commercial/industrial. Each location had a USGS gauging station at or near the sampling site. Land use was tabulated using NLCD 2001. The researchers had difficulty finding locations with homogenous land use meeting their criteria, so many of the sites had mixed land uses as a result. All of the recommended parameters were included in the monitoring, with the exception of 2,3,7,8 TCDD. At each site two baseflow events and six storm events were sampled. Detailed summary statistics, non-detect frequencies, and box and whisker plots are presented in appendices for each site. The study provides an additional source of baseflow concentrations, storm event concentration ranges, and loading rates by land use type that can be used to inform model development.

Ecology (2011) prepared a report detailing relative magnitudes of toxic chemical loads by source in support of the Phase 3 Puget Sound Toxics Loading Analysis. The report compiles data about source types and releases using "peer-reviewed literature, government and non-governmental organization publications, government databases, direct communications with experts, readily available marketing data, and other miscellaneous information resources". All of the recommended parameters were discussed, with the exception of 2,3,7,8 TCDD. The study identifies source types and relative load contributions, and includes uncertainty estimates. For instance, primary sources of arsenic are identified as air emissions, treated lumber, roofing materials, and fertilizers. Estimated loads by pathway are also provided (surface runoff, groundwater, and air deposition). While the report does not provide any direct information for model parameterization, it does help for placing loading sources in context with land uses and activities in the watershed.

Western Washington NPDES Phase I Data Report

An additional resource for characterizing toxic pollutant concentrations and loads by land use is a study of Phase 1 NPDES monitoring summarized by Ecology (2015). Flow-weighted composite storm event monitoring data were collected during 2009 – 2012 from multiple sites in King, Snohomish, Pierce, and Clark counties. A total of 597 unique storm events were sampled. Monitoring was conducted at each location for at least three years, allowing for characterization of numerous storm events. Both water quality and, to a lesser extent, storm solids or sediment were sampled. Water quality parameters included copper, zinc, mercury, cPAHs, and DEHP; in addition, dissolved arsenic was monitored at one of the sites. Solids/sediment parameters included copper, zinc,

mercury, cPAHs, DEHP, and PCBs as Aroclors. The primary land use at the sites was characterized as low-density residential (4), high-density residential (6), commercial (8), and industrial (2). However, in most cases the land uses were somewhat heterogeneous. Total impervious area is included in the site summaries. An analysis of variation by dry versus wet season is provided as well. Statistical summaries of concentrations and loads by land use are provided in report appendices. The study provides an additional source of storm event concentration ranges and loading rates by land use type that can be used to inform model development. However, the contributing land use distribution to each site should be evaluated independently; one of the "industrial" sites is actually a combination of high-density residential and commercial, and apparently has no industrial land.

Duwamish River Sediment Sampling and Analysis (Ecology)

In 2008, Ecology collected surface sediment samples and conducted an outfall survey on the Duwamish River between RM 4.9 and 7.4. Sampling focused on areas near outfalls. A total of 116 surface sediment samples (including five field duplicates) during April and May 2008.

3.3.4.6 Atmospheric Deposition

A number of atmospheric deposition studies provide information to set initial atmospheric deposition rates, and when combined with build-up washoff and sediment/solids potency will form the basis of loading rates from individual land use types. This information can also support direct atmospheric deposition loading to surface water.

King County (2013d) performed bulk air deposition monitoring in the Duwamish watershed to better understand patterns of toxic pollutant loading. Monitoring was conducted at five stations from July 2011 through Oct 2012; a sixth station was added during the study. Three of the stations were located in the LDW watershed, two were within the Lower Green River watershed, and one was located in a rural area in the Upper Green River watershed. The stations were selected to represent a gradient of development intensity reflected by surrounding land use. All of the recommended parameters were included, with the exception of DEHP. PCBs were sampled as congeners. Sampling data was converted to aerial fluxes in the report results. Summary statistics are provided for the fluxes for each of the locations. While it is not possible to distinguish between wet and dry deposition, the report does provide air deposition loading totals across a range of land uses. However, microscale differences in loadings between two stations located 0.3 miles apart were noted, suggesting that localized sources play an important role.

In a report prepared for Ecology, Leidos and Newfields (2013) provided a detailed scoping study of air deposition of toxic pollutants to the LDW. The report includes arsenic, mercury, cPAHs, PCBs, DEHP, and dioxins/furans. Using a variety of data sources, the study summaries loads to the LDW using several different classifications. Contributions from long range, regional, and local sources are tabulated. An analysis of deposition to water surfaces versus land surfaces is presented. Stationary versus mobile sources are discussed, as well as other nonpoint sources. Where possible, seasonal variation is characterized. The report concludes with a discussion of major data gaps; those relevant to watershed modeling include estimation of indirect deposition to upland areas, gas exchange, and uncertainties with air emissions data. The report provides a basis for estimating air deposition loading for the model, though there is no characterization of wet versus dry deposition.

Ecology (2010) studied air deposition of toxic pollutants in the Puget Sound region. Seven sampling stations were used to represent a range of geographic regions, precipitation patterns, and potential air pollution sources. Bulk deposition data were collected from 2008 – 2009, and included arsenic, mercury, methyl-mercury, copper, zinc, and cPAHs. Results were compared to previous studies to infer temporal changes in deposition. Summary statistics and boxplots were presented in the results. The report concluded that fluxes in the Tacoma urban/industrial area have generally decreased an order of magnitude during the past 20 years. The study has some utility for providing regional air deposition values for comparison to studies within the Duwamish watershed, and may also be useful for characterizing temporal changes in toxics deposition

King County (2004, 2005a, 2005b) report on phthalate studies in the Green/Duwamish. In an effort to identify specific sources of phthalates in storm drains and sanitary sewers, King County and City of Seattle staff created a task force with the City of Tacoma in 2003 to test commonly used materials. The task force built upon a sampling and analysis plan originally submitted to EPA by the City of Tacoma (related to the Thea Foss Superfund investigation) by adding additional materials after conducting an extensive research effort on phthalate sources. The additional products consisted of materials commonly used in the region that had not already been tested and which research suggested may be high in phthalates. While DEHP is the most prevalent phthalate in Duwamish sediments, other phthalates (6 total including DEHP), and polyaromatic hydrocarbons (PAHs, 14 total) were also analyzed.

DEHP was detected above the analytical detection limit in four liquid samples, with two other phthalates detected in six liquid samples. DEHP was more commonly detected in solid products and at higher concentrations, with serpentine belts, used cigarette butts, packing peanuts, brake pads, brake pad dust, and tires having the highest concentrations, respectively. Two other phthalates were found in detectable levels in a total of five solid products. Low or undetected DEHP levels in almost all liquid samples indicate that businesses in the Duwamish do not need to make significant changes in the cleaning and maintenance products they use, but that other potential sources may still need to be investigated. However, high levels of DEHP and other phthalates in automotive products (e.g., brake pads, belts, tires, used motor oil) suggests they may be a significant source. Additional sampling of the Tacoma Dome roof also suggested that atmospheric deposition of phthalates due to release in exhaust may be of concern and warranting further investigation.

The next phase of the phthalate source study was focused on determining whether atmospheric deposition (both “dry” and “wet”) is a significant source of phthalates in stormwater, beginning with a literature review and the development and identification of appropriate sampling methods and locations. To limit sampling cost and complexity, passive air deposition sampling was selected for this phase, rather than a combination of high-volume dry deposition samplers and wet deposition samplers that only collect samples when rainfall is occurring. A passive sampler is constantly open to collect both rainfall (wet) and some atmospheric particulates (dry). Three prototypes were laboratory tested and the samples were analyzed for phthalates with results determined to be acceptable. Passive deposition samplers were selected for use in the next phase of sampling, planned for January through April 2005, to collect aqueous samples from four stations identified in the LDW.

In this phase, four rounds of atmospheric samples were collected using passive deposition samplers between January and May 2005 at four sampling locations in the Lower Duwamish: three in the Duwamish Valley and one on Beacon Hill. Stations were selected to collect neighborhood-scale samples from different regions of the Lower Duwamish drainage area. Results for air deposition flux (µg/m²/day) are presented, corrected for blank contamination. For three of the four rounds of sampling, samplers were in the field for 22-36 days. Round 3 samplers were only in the field for seven days, so results for this round are considered less useful. Rounds 1 and 2 occurred during winter and Rounds 3 and 4 occurred during spring.

Analyzed constituents included seven PAHs, pyrene, benzo(g,h,i)perylene, and six phthalates (including BEHP). Sample results showed DEHP concentrations were typically lowest at Beacon Hill, so the researchers developed ratios of DEHP concentrations at the other three stations relative to Beacon Hill for comparison. Results are presented for all four rounds. Ratios of the three Duwamish Valley stations to Beacon Hill were higher in winter than in spring, which is consistent with historic Puget Sound Clean Air Agency data. The results were also compared with other studies in the same airshed (Georgia Basin) and other regions (Great Lakes and Denmark) as a quality check. The study authors note that (1) the amount of atmospheric particulates can play an important role but there is currently insufficient data to make correlations, and (2) additional air deposition testing is needed, both to evaluate the reproducibility of results and to facilitate correlations with particulate concentrations and other atmospheric measurements.

3.4 SUMMARY OF GAPS AND STRATEGIES – WATERSHED MODEL

Key sources described in the Technical Approach were:

1. Urban runoff and associated loads (of sediment, solids and pollutants),
2. Agricultural runoff and associated loads,
3. Other runoff such as from natural areas and associated loads,
4. Atmospheric deposition, including spatial variation in deposition rates,
5. Groundwater contributions to both watershed-based streams and to the LDW directly.
6. Point source discharges (industrial, regulated stormwater outfalls, etc.),
7. Spills and/or leaks (contaminated sites and industrial operations areas contributing high contaminant loads),
8. Legacy COCs in bed sediments above the LDW,

Many of the candidate pollutants (with exception of DEHP, Cu, Zn, arsenic, and some forms of mercury) are strongly sorbed to sediments and thus the ability to simulate sediment/solids loading, together with the potency (mass per mass of sediment) is key to simulating these compounds in the watershed. LSPC has a capability to simulate sediment loading, and parameters can be associated with soil properties available in the USDA SSURGO database. Solids accumulation and washoff from urban impervious surfaces is also relatively well documented. In addition, the available WRIA 9 models are already calibrated for solids/sediment, including scour, deposition, and transport in stream channels. Potency data are less readily available and are likely to reflect site-specific circumstances (e.g., industrial areas where PCBs were used). The LDW source control-related reports from Ecology will be useful for some of the more polluted areas.

Atmospheric deposition (item #4) to land units is applied on top of land-based buildup parameters and is informed by recent King Co. monitoring efforts. Groundwater contributions (item #5) are associated with pervious land units, but are less significant for pollutants that sorb strongly to sediment. Existing LDW sediment stores of the main COCs have been described in detail in the RI/FS. Table 22 provides a summary of data by parameter to support model development for these sources and pathways.

Table 22. Summary table of data/study by parameter - land use/land cover-based loading rates

Parameter	Surface Runoff/Shallow Groundwater *	Atmospheric Deposition *
Solids and Sediment	USGS National Water Quality Assessment (1994-2003) King County (2014) King County (suspended solids study) King County (2015) Herrera (multiple citations)	--
PCBs	Herrera (multiple citations) Ecology (2015)	King County (2013d) Leidos and Newfields (2013)
cPAHs	Herrera (multiple citations) Ecology (2015)	King County (2013d) Leidos and Newfields (2013) Ecology (2010)

Parameter	Surface Runoff/Shallow Groundwater *	Atmospheric Deposition *
2,3,7,8 TCDD	(King County, 2014 provides 5 stations at major tributary outlets)	King County (2013d) Leidos and Newfields (2013)
DEHP	Herrera (multiple citations) Ecology (2015) King County (2004, 2005a, 2005b)	King County phthalate studies (2004, 2005a, 2005b) Leidos and Newfields (2013)
Arsenic	Herrera (multiple citations) Ecology (2015)	King County (2013d) Leidos and Newfields (2013) Ecology (2010)
Copper	Herrera (multiple citations) Ecology (2015)	King County (2013d) Ecology (2010)
Zinc	Herrera (multiple citations) Ecology (2015)	King County (2013d) Ecology (2010)
Mercury	Herrera (multiple citations) Ecology (2015)	King County (2013d) Leidos and Newfields (2013) Ecology (2010)

* Leidos (2014) provides a compilation that may also provide additional supporting information.

Once land use based-loading rates are initially captured in the model calibration process, the instream water quality model is calibrated at larger scales (e.g., by tributary subwatershed and then by the main sections of the mainstem of the Green River (e.g., Upper, Middle, Lower). Table 23 summarizes data available for instream water quality calibration. Additional data relevant to this effort are still being collected.

Table 23. Summary table of data/study by parameter and watershed area – instream calibration

Parameter	Upper Green River Watershed	Middle Green River Watershed	Lower Green River Watershed
Solids and Sediment	King County (2015) USGS National Water Quality Assessment (1994-2003)	King County (2014) USGS National Water Quality Assessment (1994-2003) King County (suspended solids study)	King County (2014) King County (suspended solids study) USGS National Water Quality Assessment (1994-2003) USGS (Tukwila monitoring) Ecology (2009)
PCBs	King County (2015)	King County (2014) King County (suspended	King County (2014) King County (suspended solids

Parameter	Upper Green River Watershed	Middle Green River Watershed	Lower Green River Watershed
		solids study)	study) USGS (Tukwila monitoring) Ecology (2009)
cPAHs	King County (2015)	King County (2014) King County (suspended solids study)	King County (2014) King County (suspended solids study) USGS (Tukwila monitoring) Ecology (2009)
2,3,7,8 TCDD		King County (2014) King County (suspended solids study)	King County (2014) King County (suspended solids study) USGS (Tukwila monitoring) Ecology (2009)
DEHP		King County (2014) King County (suspended solids study)	King County (2014) King County (suspended solids study) USGS (Tukwila monitoring)
Arsenic	King County (2015)	King County (2014) King County (suspended solids study)	King County (2014) King County (suspended solids study) Ecology (2009)
Copper		King County (suspended solids study)	King County (suspended solids study) USGS (Tukwila monitoring)
Zinc		King County (suspended solids study)	King County (suspended solids study) USGS (Tukwila monitoring)

Parameter	Upper Green River Watershed	Middle Green River Watershed	Lower Green River Watershed
Mercury		King County (suspended solids study)	King County (suspended solids study) USGS (Tukwila monitoring)

The recent data collected by a number of agencies begins to fill keys gaps in the data identified by the RI/FS and Leidos (2014). These recent data combined with the earlier, more limited data provide a solid basis for watershed model development for nearly all of the prioritized parameters. The largest gap is for dioxins/furans (e.g., 2,3,7,8 TCDD). Data collection has been limited relative to the other constituents. Where it has been conducted, detections in the water column are rare (e.g., USGS). Additional sampling is recommended for this parameter to support development of a robust model in the long term; however, initial scoping-level modeling may inform future model enhancements and data collection.

A review of Table 23 suggest some gaps in the Upper Green River above the dam for instream water quality data, especially for certain parameters (i.e., copper, zinc, mercury, DEHP, and 2,3,7,8 TCDD). However, the significance of the gap should be understood relative to the significance of the area as a source of COCs. This is a relatively undeveloped and mostly protected area and is unlikely to be a major source of COCs below the dam. Atmospheric deposition is likely a primary source of COCs and these fluxes can likely be well constrained with the existing atmospheric deposition data. Uncertainties will remain but are not considered a barrier to a credible model.

Point sources (#6) in the watershed (excepting MS4 stormwater permits) that are monitored and discharge to surface waterbodies directly will be input into the model at a minimum of monthly average or up to daily frequencies according to data availability. Inputs for point sources typically includes Flow Volume and either loads or concentrations. Not all point sources have been monitored for all constituents that are needed for model input. Filling of missing data is conducted in three general ways. First, if there are gaps in the data that are three months or less, an average will be calculated from before and after gap months. Second, if the gaps in the data are larger than three months the long term monthly average will be supplied. Lastly, if no information for a particular constituent that is required for the model exists then a default assumption will be utilized. Default assumptions will be developed in consultation with project team members. Data for these types of point sources, from a modeling perspective is not considered a significant gap at this time.

Source control studies conducted to date and information gathered in Leidos (2014) will help to support characterizations of #7 in the earlier list of sources, “spills and/or leaks (contaminated sites and industrial operations areas contributing high contaminant loads).” Legacy COCs (#8) in bed sediments above the LDW can be informed by the RI/FS as well as studies by Ecology, King County, and USGS described earlier. However, in all these cases, the heterogeneity and temporal variability of these sources will be a challenge for developing a watershed scale model.

For the watershed, earlier PCB data were collected as Aroclors and more recent collection focused on congener data (from which homologs may be inferred). As discussed in the LDW section of this memo, use of Aroclor data is somewhat problematic for weathered environmental samples. While the original congeners of Aroclor-1260, for example, are present in approximate ratios (or percentages), once released to the environment, shifts may occur in the ratios of congeners present in an environmental sample. However, it is assumed that this degradation occurs to a lesser degree in the watershed compared to the LDW.

Development of a watershed model can proceed with all of the prioritized parameters. In the case of the dioxin/furan, initial model development would be focused on understanding model sensitivity to inform what gaps are important. For other parameters, while data is deemed sufficient for initial model configuration and calibration, the data sets to support instream calibration do not span long periods of time. Therefore, additional data collection to support additional validation exercises is recommended.

Knowledge gaps and options relative to the watershed model are summarized in Table 24.

Table 24. Summary of knowledge gaps and options for watershed model

Knowledge Gap	Options and Recommendations
Limited data for dioxins/furans in general	Options: 1. Do not model dioxins/furans in the watershed 2. Pursue additional data collection prior to modeling 3. Use model to develop a preliminary analysis of key dioxins/furans Recommendation: A combination of options 2 and 3 should be pursued. The watershed model should be used to develop a preliminary scoping analysis of dioxins/furans (focusing on 2,3,7,8-TCDD as a surrogate) using an approach similar to PCBs. This scoping model can be used to conduct sensitivity analyses to guide additional data collection needs for an eventual comprehensive model of these constituents.
Limited data for copper, zinc, mercury, and DEHP in the Upper Green River	Options: 1. Collect additional data prior to modeling 2. Assume loads are driven by geology and/or atmospheric deposition and proceed with modeling. Recommendation: Option 2 is recommended because loads are expected to be small from this relatively undeveloped area. Sensitivity analyses with the model can be used to determine the value of additional information.
Poor status of existing TSS calibrations in certain subbasins	Options: 1. Use existing calibrated parameters 2. Expend effort to improve calibration Recommendation: Because movement of sediment is key to the movement of sediment/solids-sorbed pollutants, effort should be expended to improve the existing TSS calibration.
Need for further instream watershed data for parameters in general to support model validation	Options: 1. Collect additional data prior to modeling 2. Proceed with model calibration and collect additional data to support further validation in the future Recommendation: Option 2 is recommended. While data is deemed sufficient for initial model configuration and calibration, the data sets to support instream calibration do not span long periods of time. Sensitivity analyses with the model can be used to inform additional data collection.

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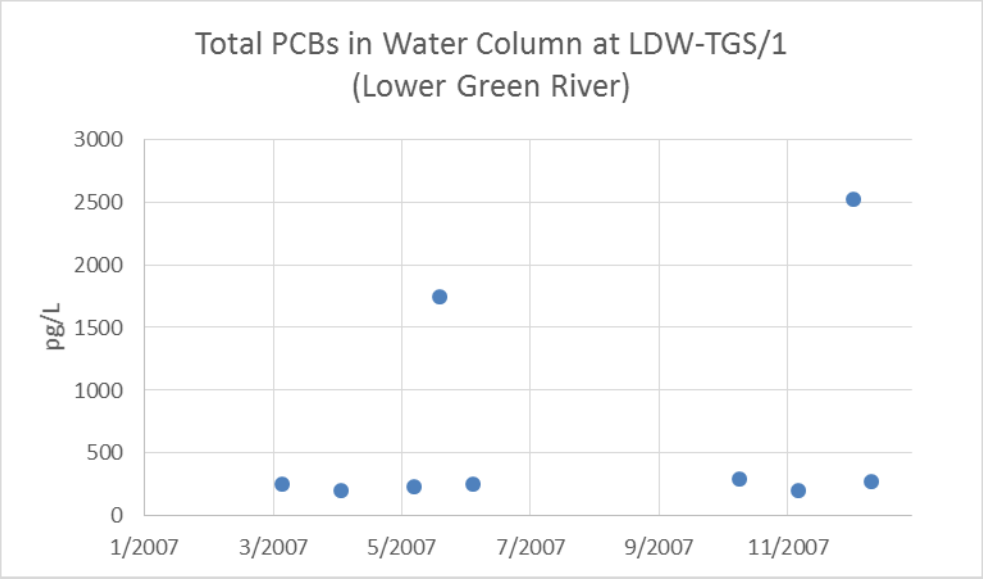
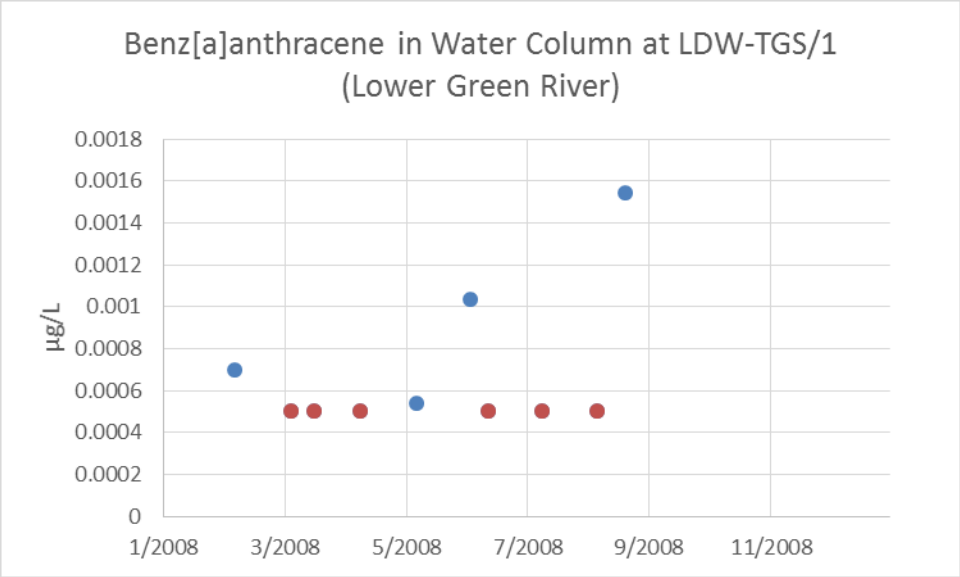
5.0 APPENDIX A.



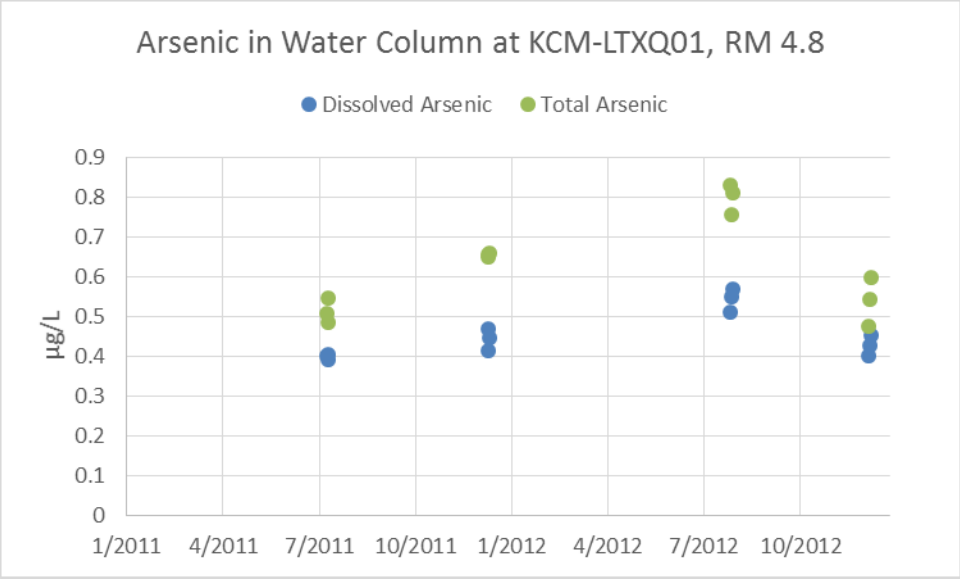
Total PCBs in Water Column at Site LDW-TGS/1, Lower Green River

(Note: Total PCBs as sum of congeners. In many cases, individual congener values were below the detection limit.)

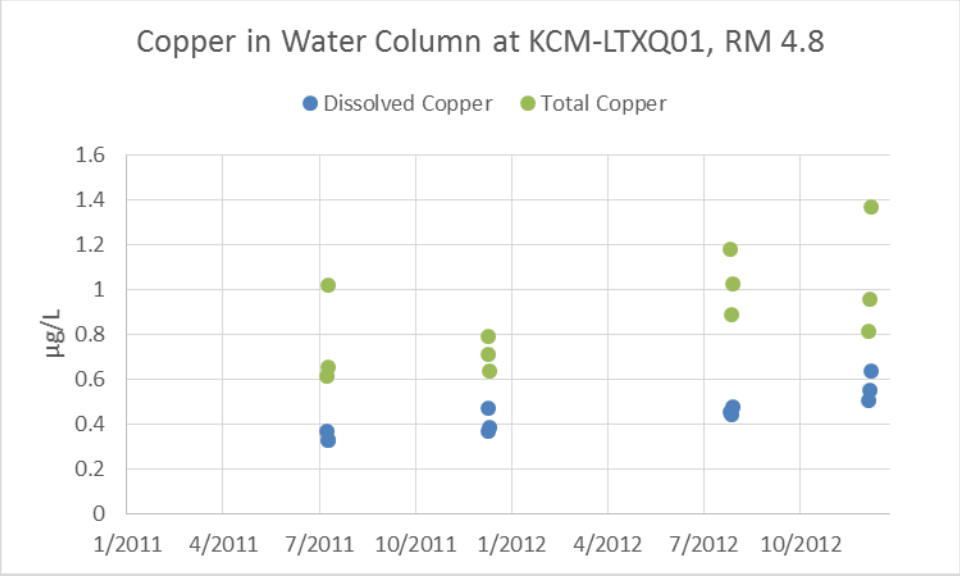


Benz(a)anthracene in Water Column at Site LDW-TGS/1, Lower Green River

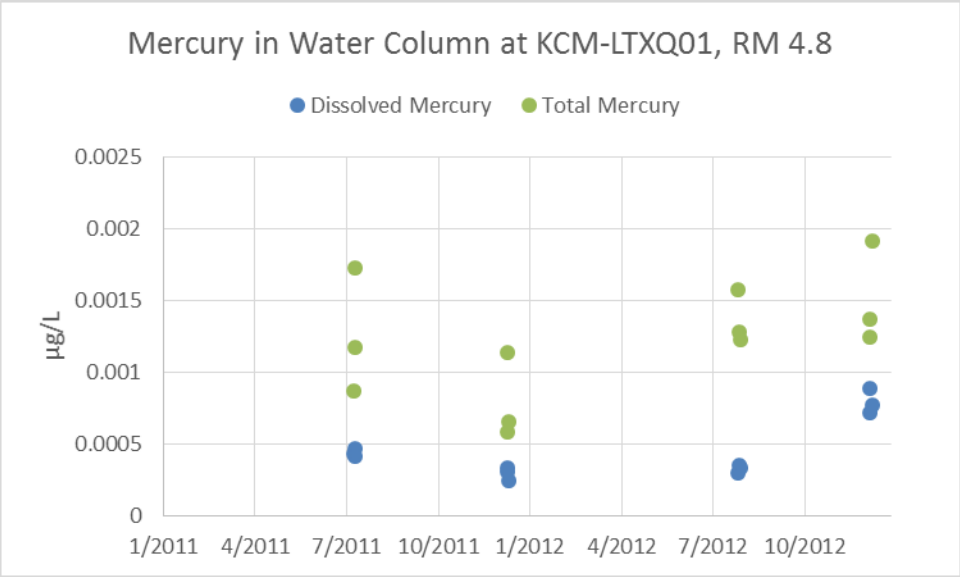
(Note: Values reported below detection limit shown in red)



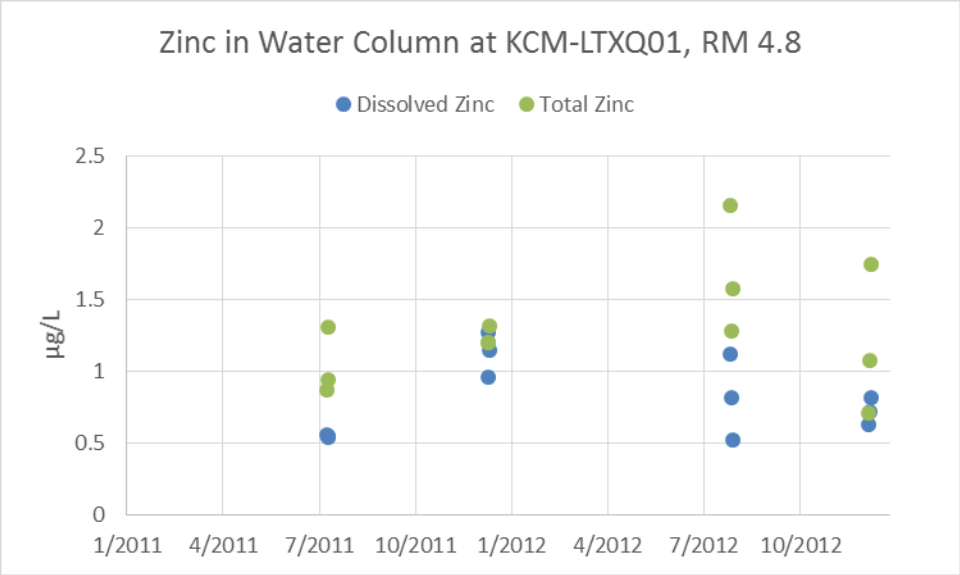
Arsenic in Water Column at Site KCM-LTXQ01, RM4.8



Copper in Water Column at Site KCM-LTXQ01, RM4.8

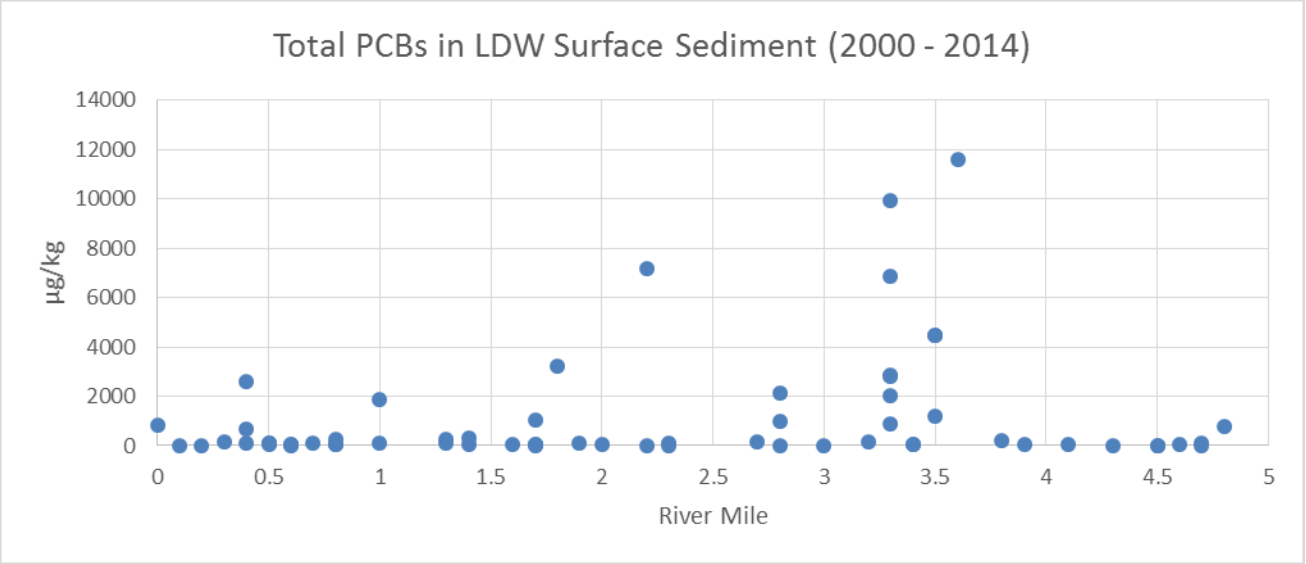


Mercury in Water Column at Site KCM-LTXQ01, RM4.8



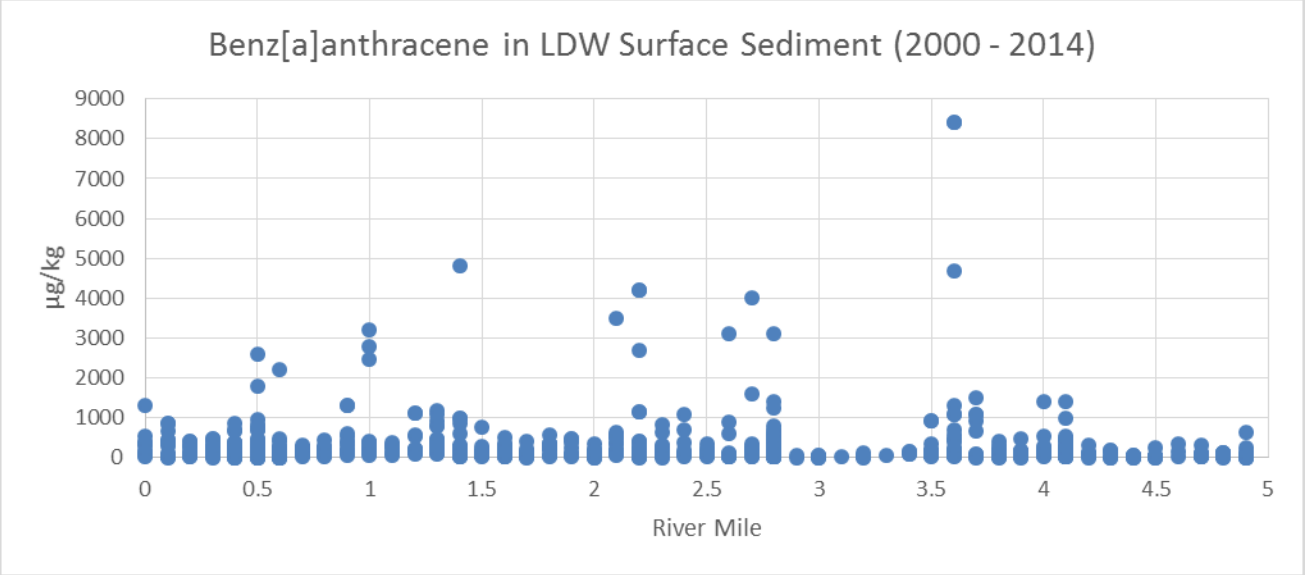
Zinc in Water Column at Site KCM-LTXQ01, RM4.8

6.0 APPENDIX B.



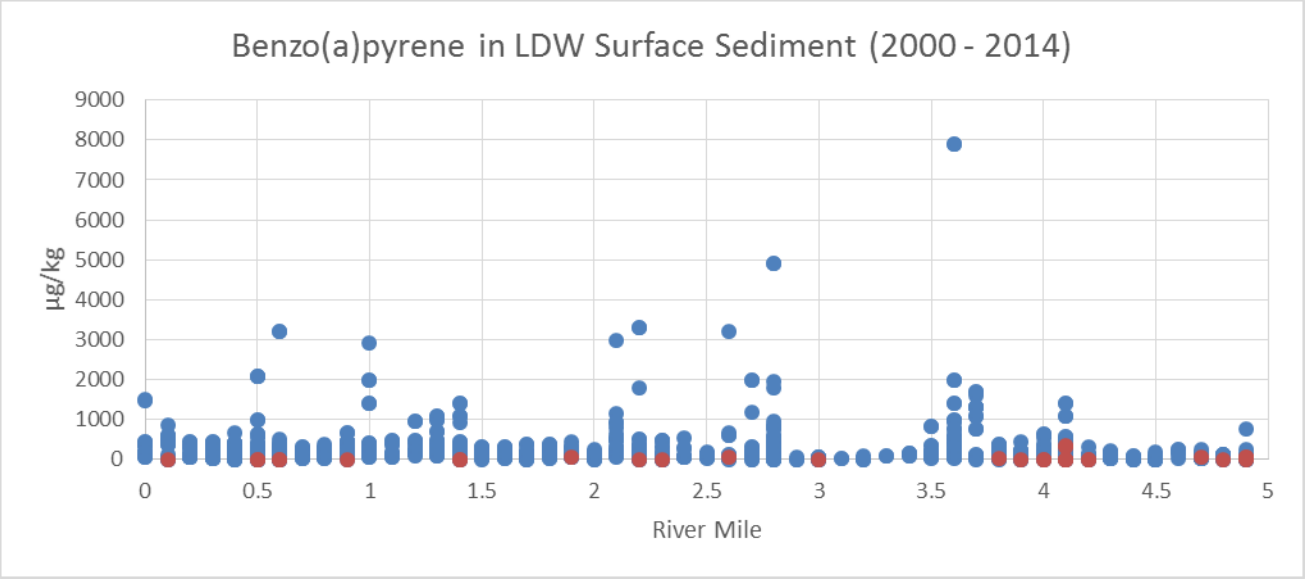
Longitudinal Plot of Total PCBs in LDW Surface Sediment

(Note: Total PCBs as sum of congeners. In many cases, individual congener values were below the detection limit.)



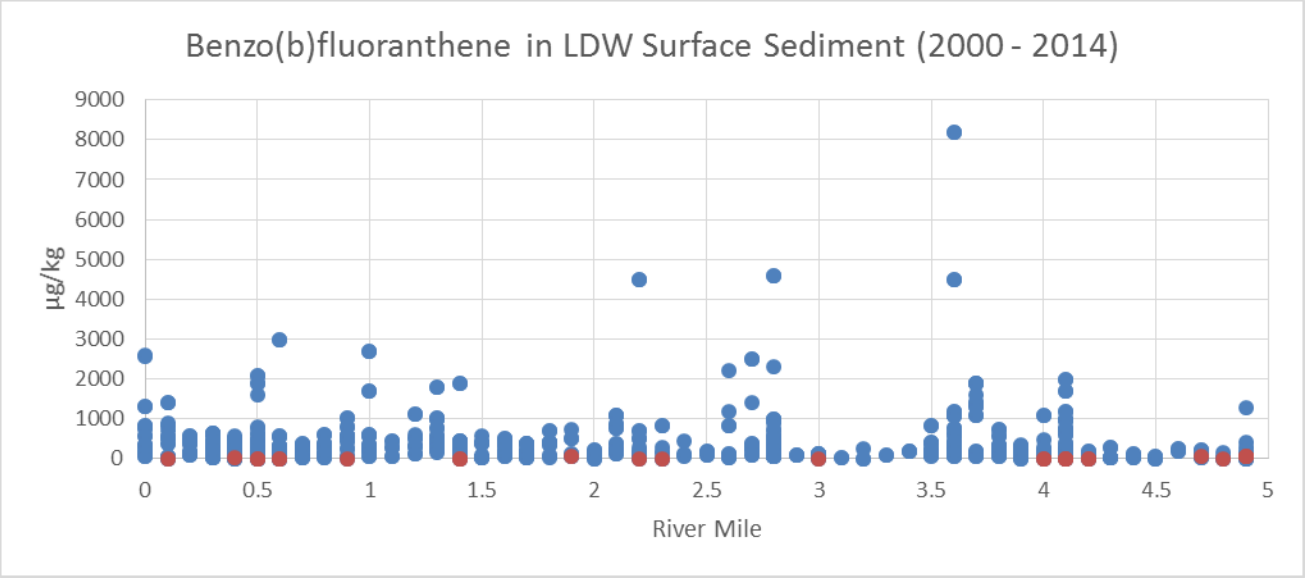
Longitudinal Plot of Benz(a)anthracene in LDW Surface Sediment

(Note: All values were above the detection limit)



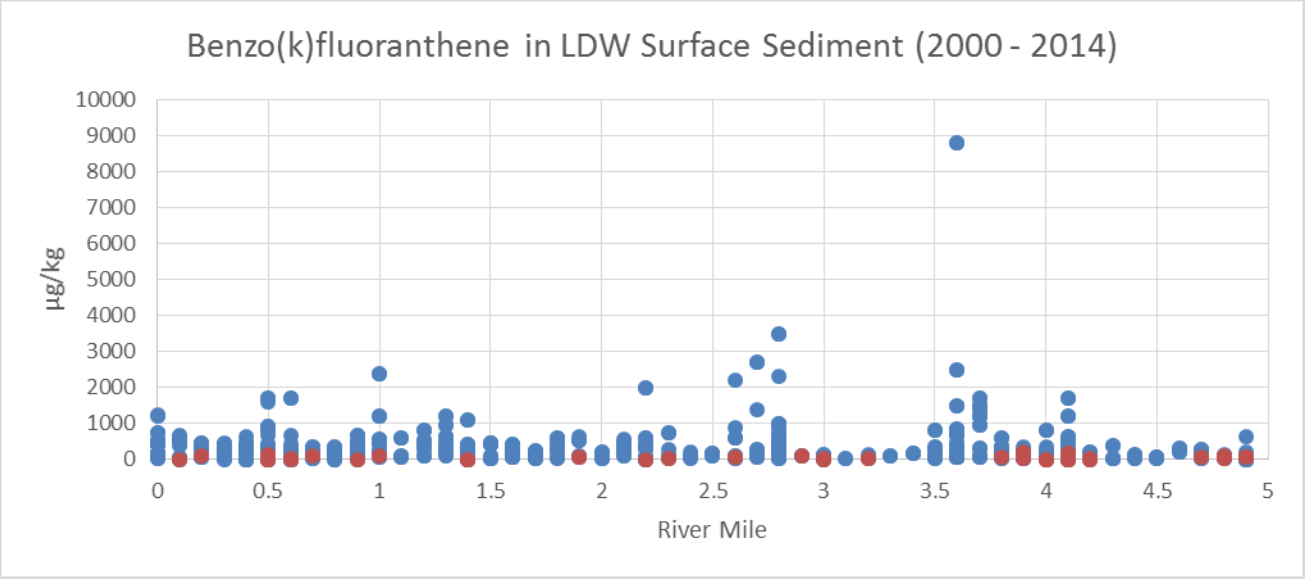
Longitudinal Plot of Benzo(a)pyrene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



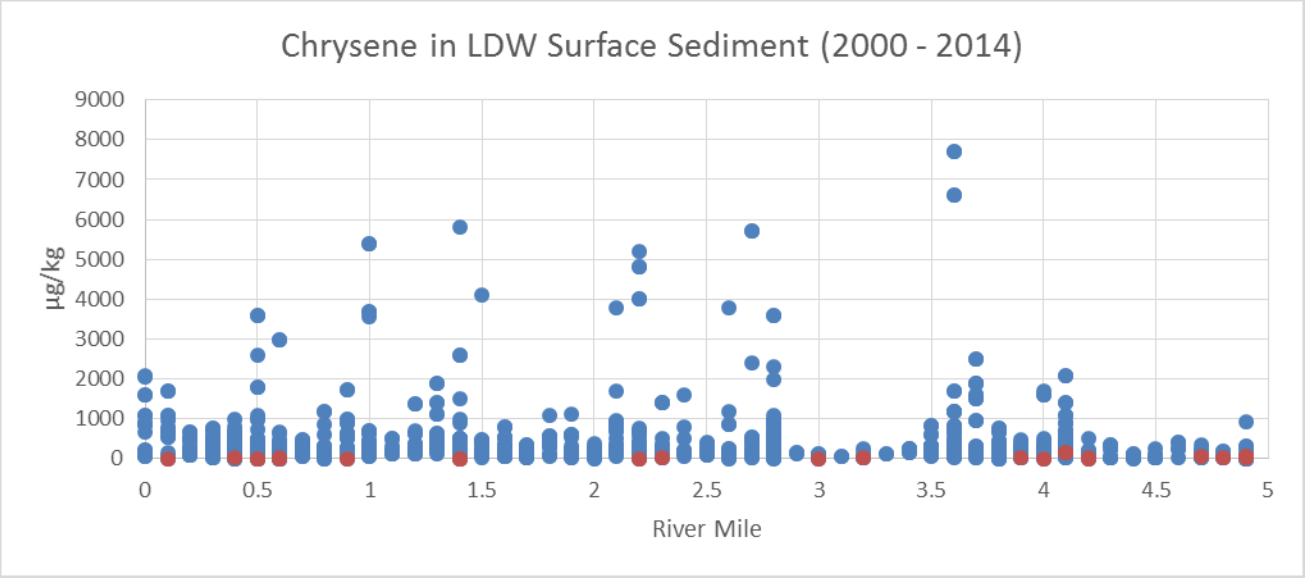
Longitudinal Plot of Benzo(b)fluoranthene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



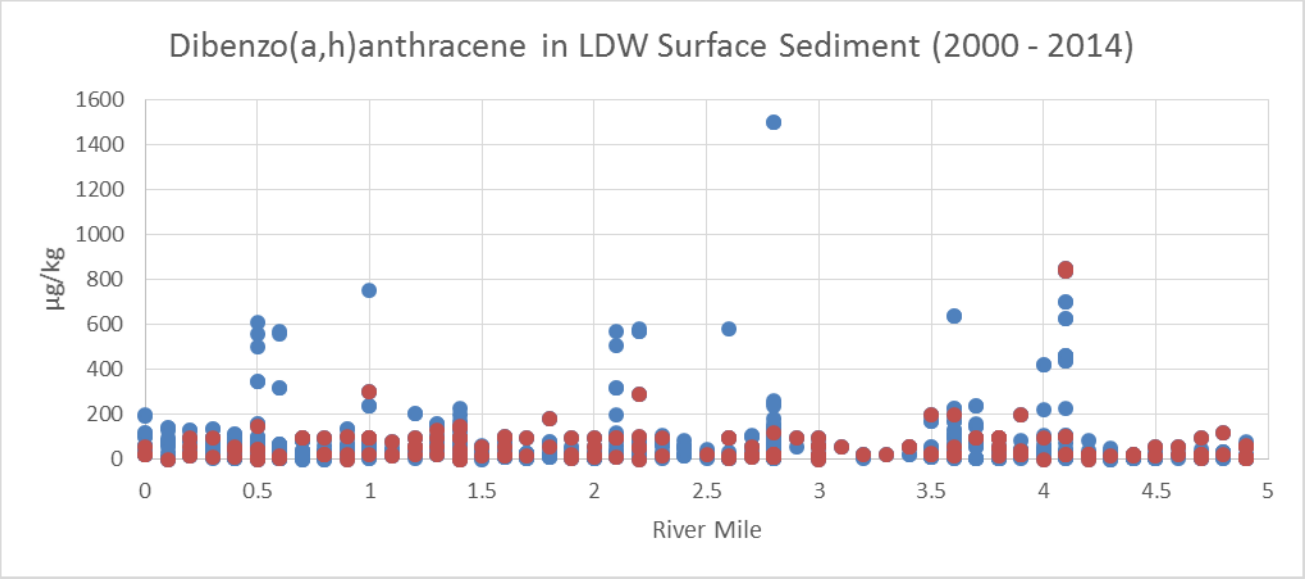
Longitudinal Plot of Benzo(k)fluoranthene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



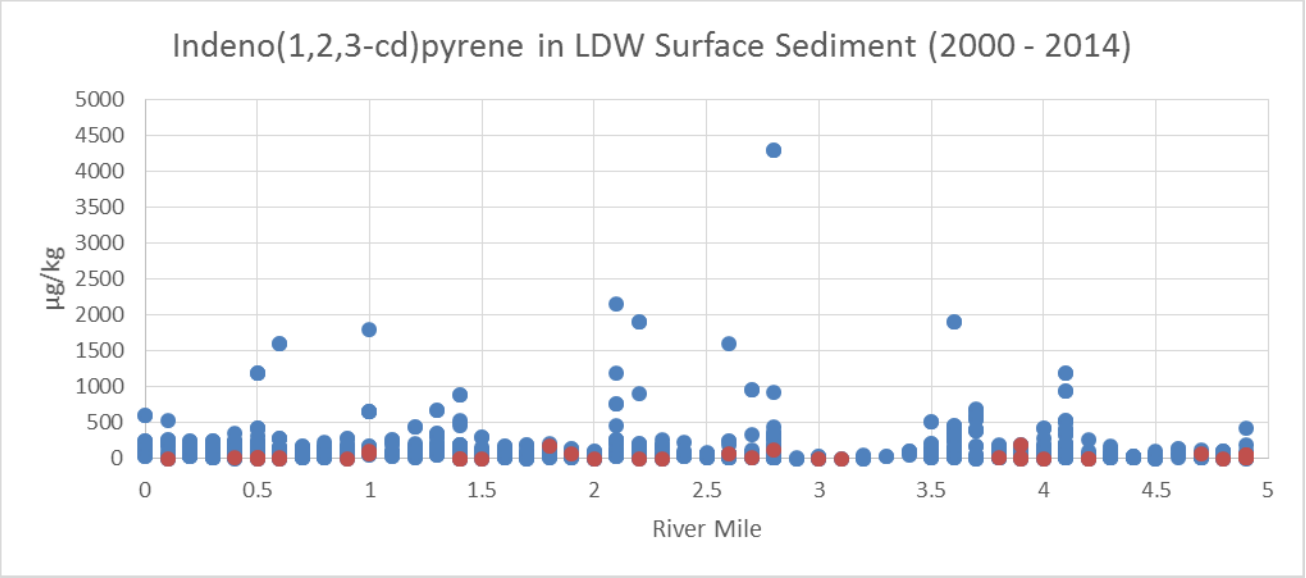
Longitudinal Plot of Chrysene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



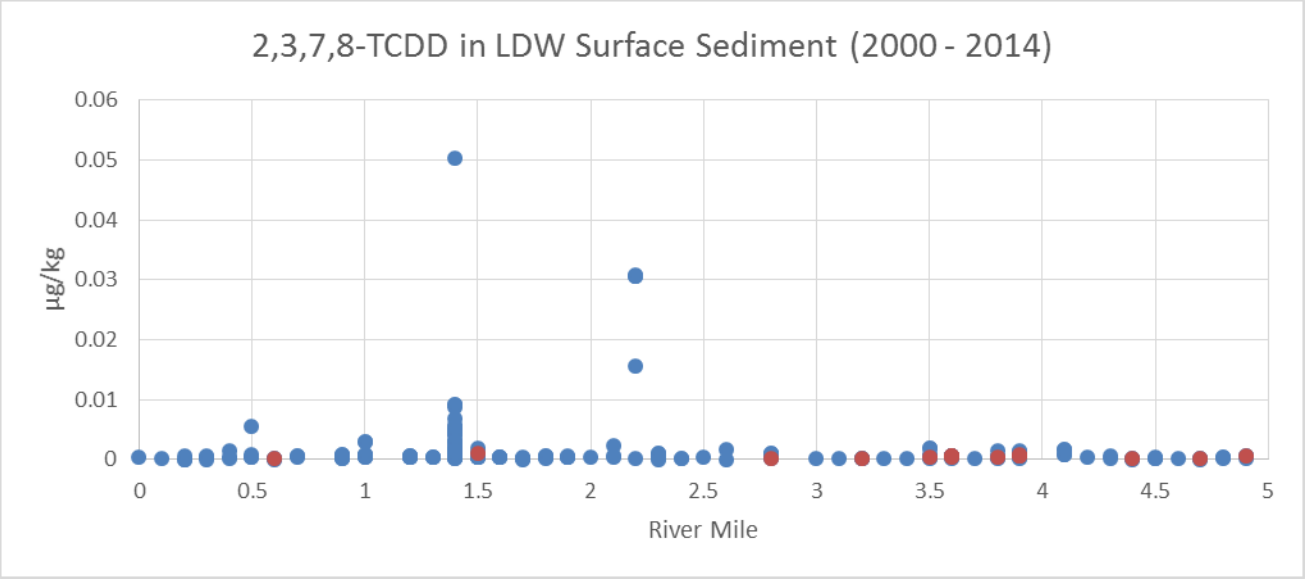
Longitudinal Plot of Dibenzo(a,h)anthracene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



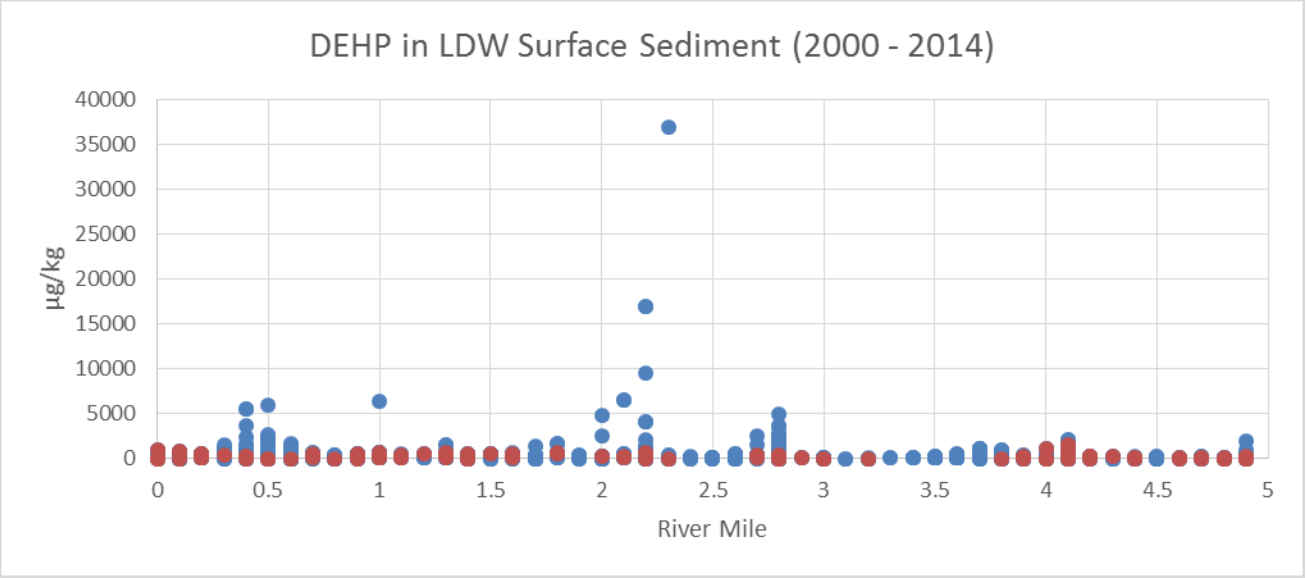
Longitudinal Plot of Indeno(1,2,3-cd)pyrene in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



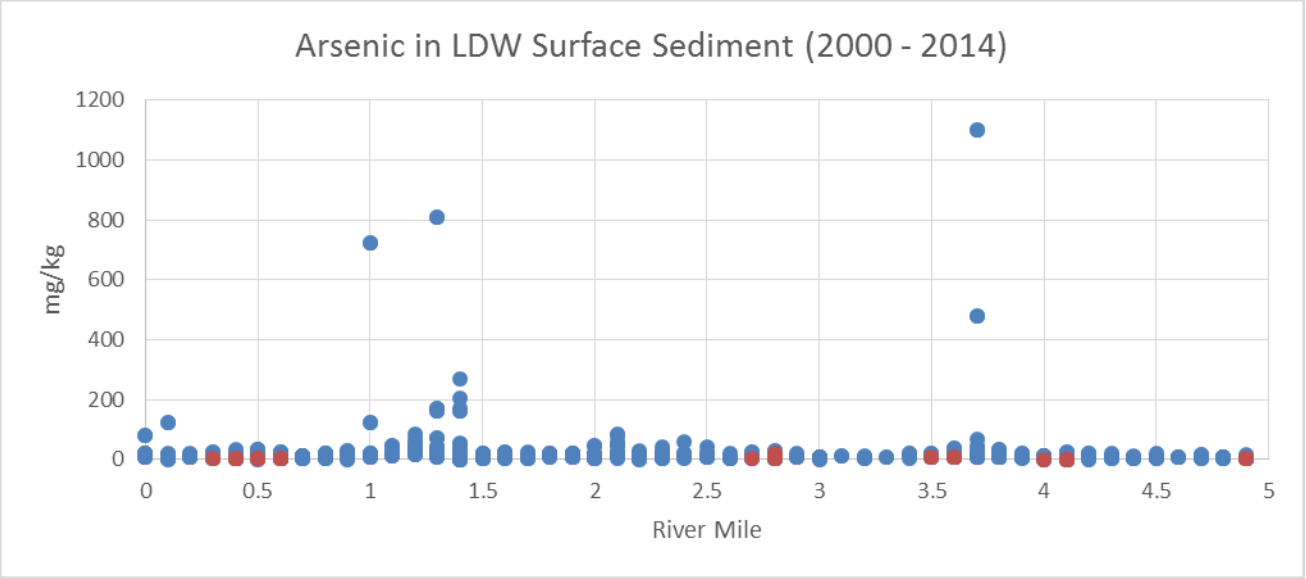
Longitudinal Plot of 2,3,7,8-TCDD in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



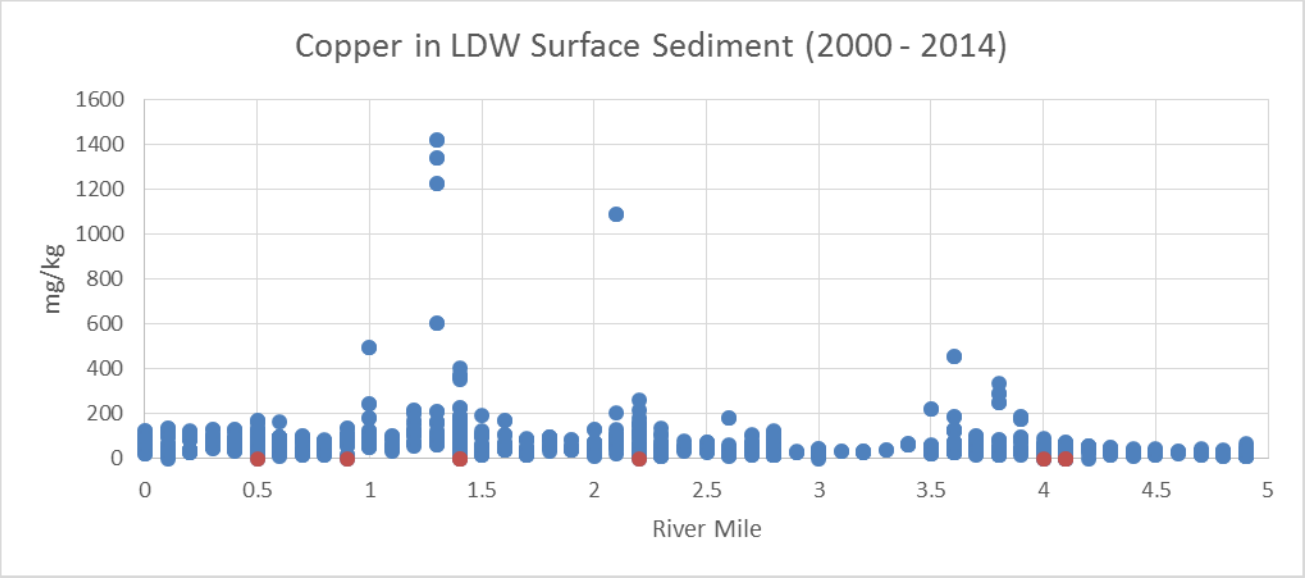
Longitudinal Plot of DEHP in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



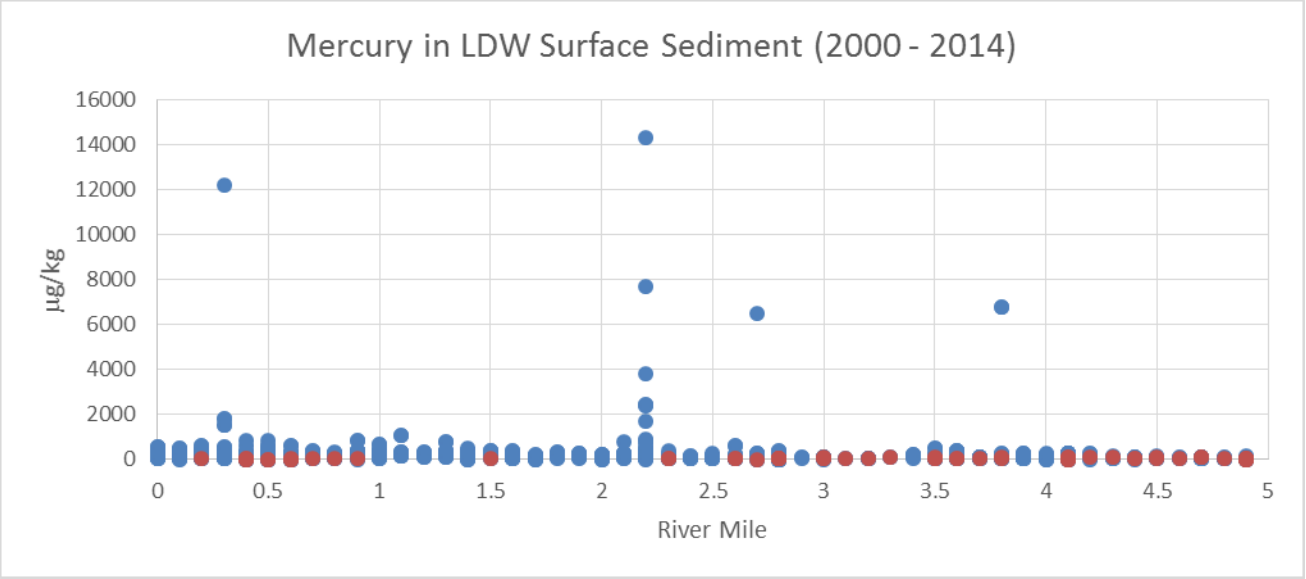
Longitudinal Plot of Arsenic in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



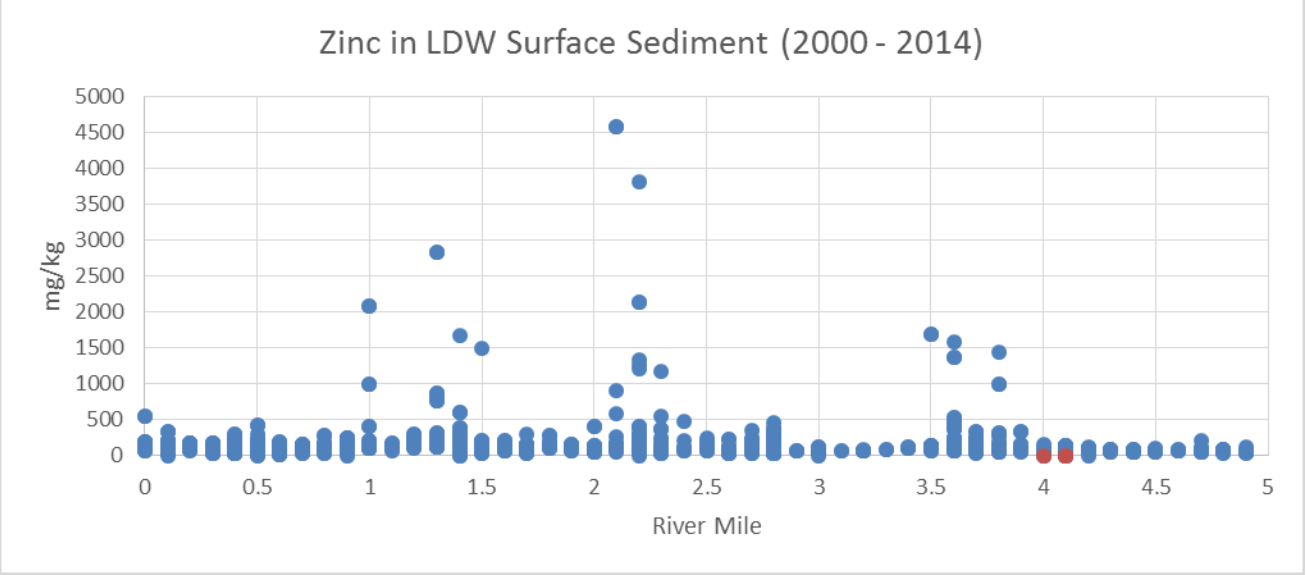
Longitudinal Plot of Copper in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



Longitudinal Plot of Mercury in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)



Longitudinal Plot of Zinc in LDW Surface Sediment

(Note: Values reported below detection limit shown in red)