GREEN-DUWAMISH POLLUTANT LOADING ASSESSMENT
TECHNICAL ADVISORY COMMITTEE

April 16, 2015

Meeting 4

DEPARTMENT OF ECOLOGY
State of Washington

EPA

TAC Meeting 4 Agenda

Time	Topic
9:00 am	Welcome & introductions
9:10 am	Preliminary model parameters
9:30 am	King County data presentation
10:30 am	Break
10:45 am	Overview of data gaps and pollutant groupings memo
11:40 am	Comments from audience
11:55 am	Next steps
12:00 pm	Adjourn

Preliminary model parameters

Criteria Used to Reduce the List of Chemicals

Tier 1

- Focus on Toxics
- CWA impairments
- CERCLA human health and ecological risk drivers
- Does the chemical bioaccumulate (Kow>5)
- Chemical linked to fish tissue consumption advisory

Tier 2

- Chemical linked to endangered species concerns
- Is there a sediment recontamination concern
- Do we have data to support modeling
- Can the chemical be simulated with the proposed models
- Can the chemical represent similar chemicals in terms of sources and pathways

Preliminary List of Chemicals for Modeling

Recommended Chemicals for Modeling Listed in order of priority				Location							
				LDW			Green-Duw River			Fish Advisory	
Parameter	Fate and Transport	Food Web	Justification	Water	Sed	Tissue	Water	Sed	Tissue	LDW	Green-Duw River
PCBs	Y	Y	High concern to both WQ and CERCLA, accumulate in biota, fish consumption advisory, recontamination potential		x	x			x	x	
cPAHs (listed below)	Y	Y	High concern to both WQ (most 303d listings) and CERCLA, accumulate in biota, ecological concern, recontamination potential		x	x					
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			x					
Arsenic (inorganic?)	Y	N	Concern for both WQ and CERCLA- natural sources in watershed		x	x					
Phthalates (Bis-2EH phthalate)	Y	Y	Primarly concern for CERCLA, recontamination potential, accumulates in biota- surrogate for other phthalates		x	x					
Copper	Y	N	Aquatic toxicity concern for ESA species- indicator for built environment		x						
Zinc	Y	N	Aquatic toxicity concern for ESA species- indicator for built environment		x						
Mercury	Y	?	Limited 303d listings, concern for CERCLA, statewide fish consumption advisory, natural sources in watershed- Not sure this chemical can be modeled on using same models		x					x	x

cPAHs= benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h) anthracene, indeno(1,2,3-cd) pyrene

Parameter questions

- Are there other factors that should be considered in selecting parameters to be modeled?
- Are there other parameters that should be evaluated in the matrix that are not on the list?
- Are there any parameters on the prioritized list that should be removed/de-prioritized? If so, why.

King County data presentation

King County Source Control Studies in Support of Lower Duwamish Waterway Cleanup

Debra Williston and Jenée Colton
Science and Technical Support Section,
Water and Land Resources Division, King County DNRP

Green-Duwamish Pollutant Loading Assessment
Technical Advisory Committee
April 2015

King County Source Control Studies

WTD's Sediment Management Program Funded ($6M) to help inform future source control efforts and monitoring methods in the Lower Duwamish Waterway

- Bulk Air Deposition Study
- Green River Studies
  - Whole Water
  - Stream Sediments
  - Suspended Solids
- CSO Basin Studies
- Duwamish CSO Source Tracing

◦Past and present studies at:

◦http://www.kingcounty.gov/environment/ wastewater/Duwamish-waterway/PreventingPollution/PollutionSources.aspx

Atmospheric Deposition of Contaminants in the Green/Duwamish River Watershed

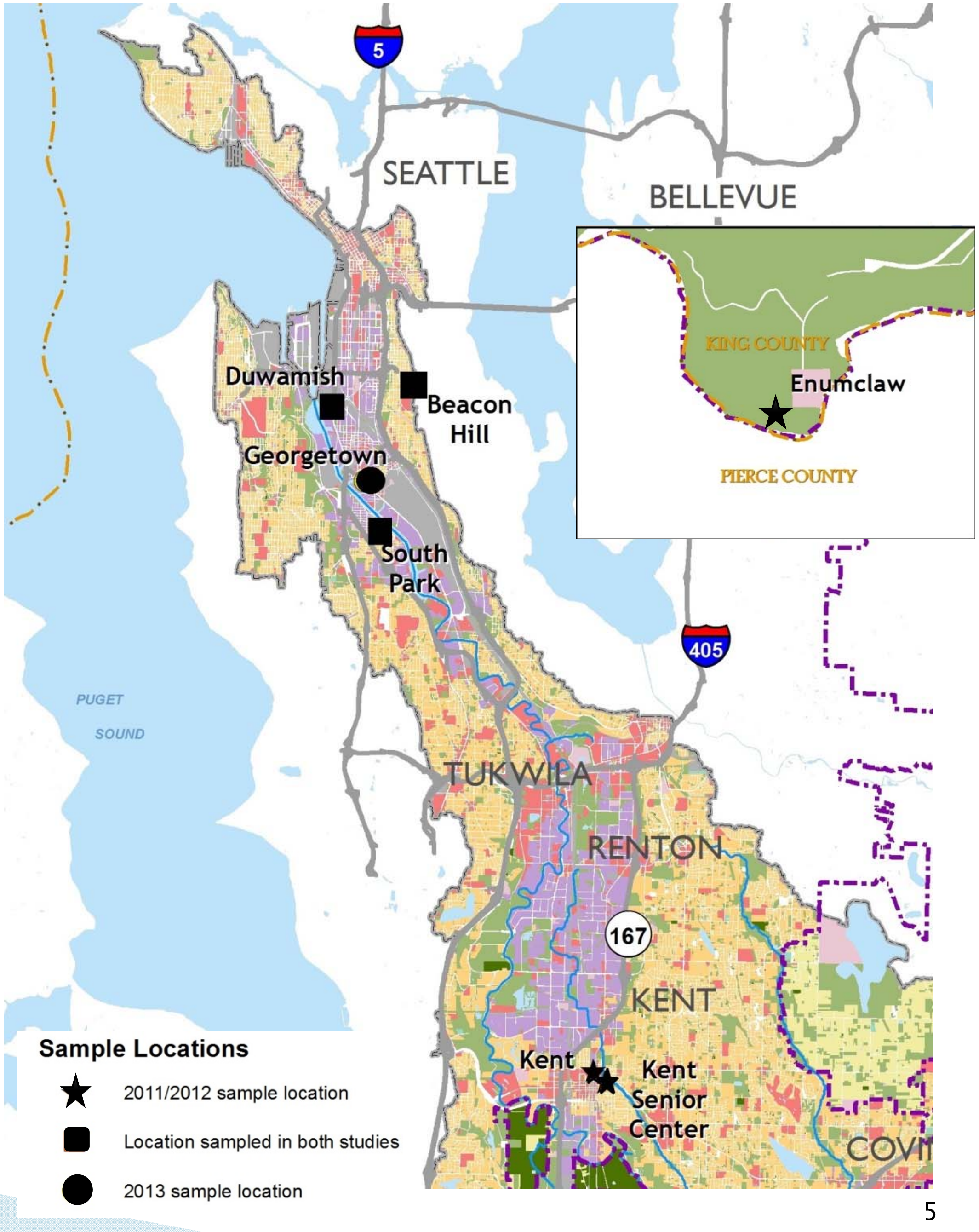
Jenée Colton
Carly Greyell
Richard Jack

Study Objectives

- Compare bulk atmospheric deposition rates in areas of different land use and urban development within the Green/Duwamish River Basin
- To provide information to assist in understanding atmospheric sources to the Lower Duwamish Waterway

Study Design

Site	Land use
Duwamish	Urban industrial
Beacon Hill	Regional urban, residential
Georgetown	Urban industrial, commercial, residential
South Park	Urban industrial, commercial, residential
Kent downtown	Suburban & commercial (with rail)
Kent Senior Center	Suburban & commercial (without rail)
Enumclaw	Rural



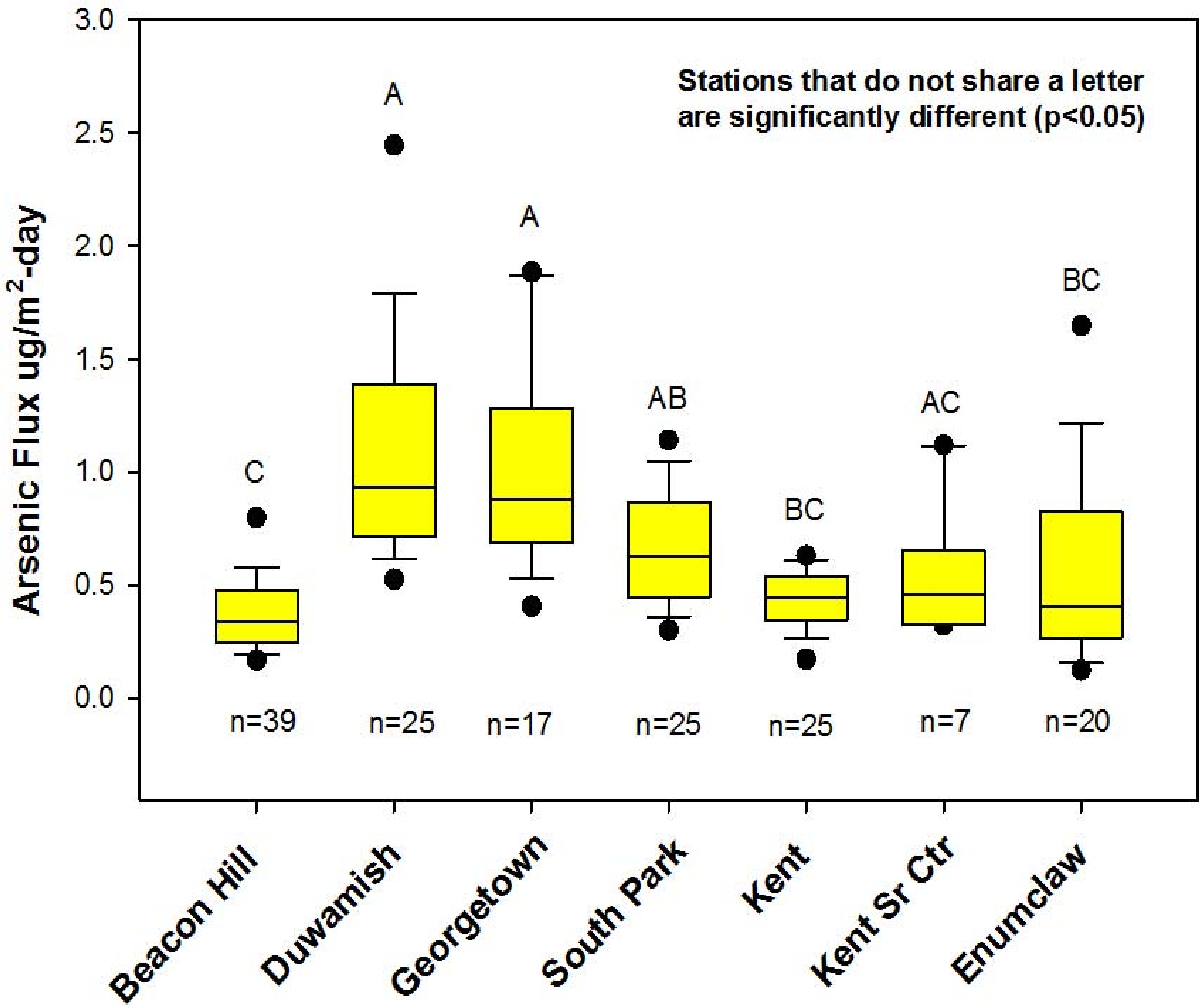
Study Design

Passive Sampler – Similar to Puget Sound Battelle Study

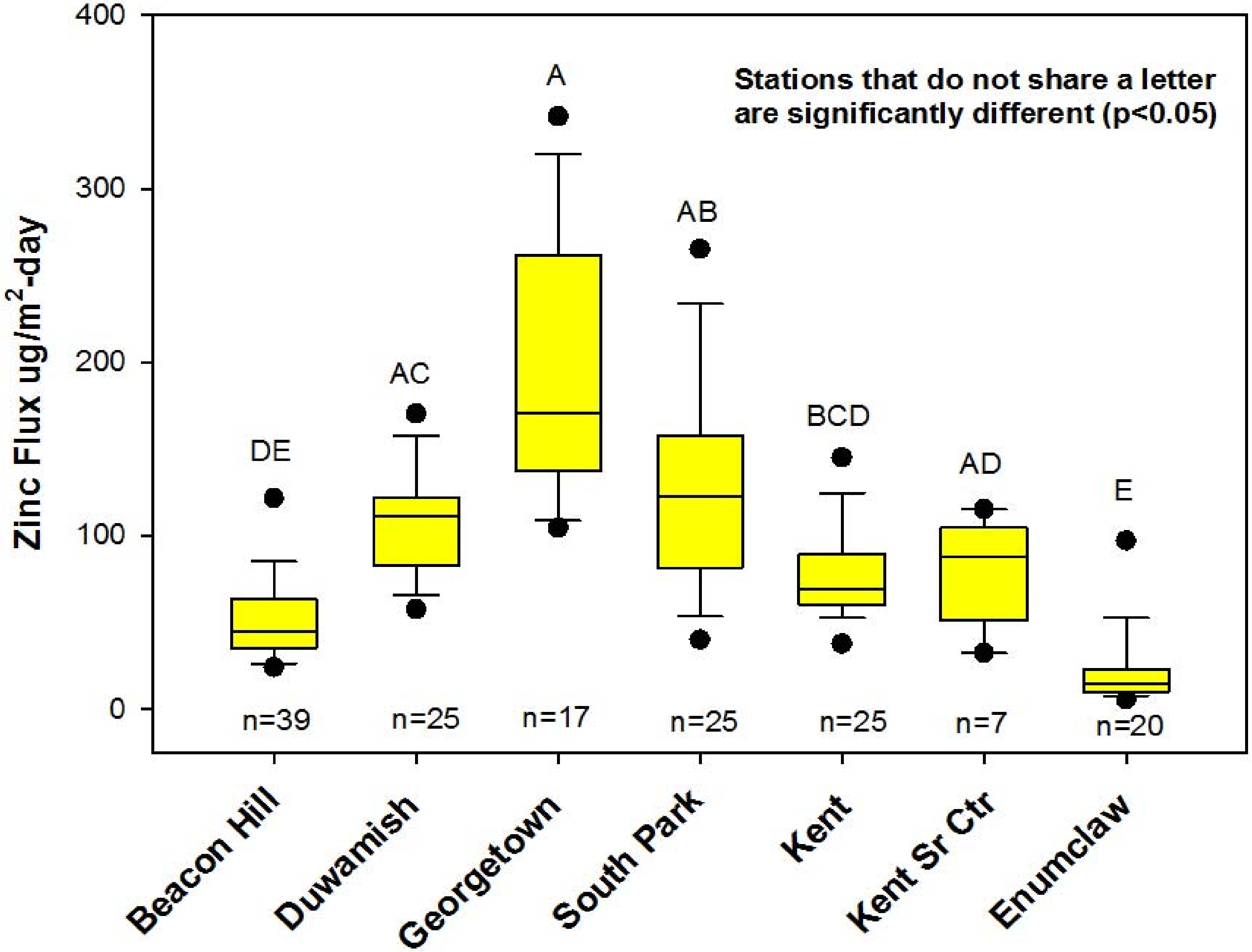
Study Design

- Analytes: metals (including mercury), PAHs, PCB congeners, dioxin/furan congeners
- Schedule
  - Metals, mercury, PAHs: continuous sampling August 2011 for approx 14 months; April through December 2013.
  - PCBs, Dioxin/furans: intermittent due to high analytical cost; over same time periods
  - Samples deployed ~2 weeks during wet season, ~4 weeks during dry season
  - Targeted ending deployment before sample containers overflowed

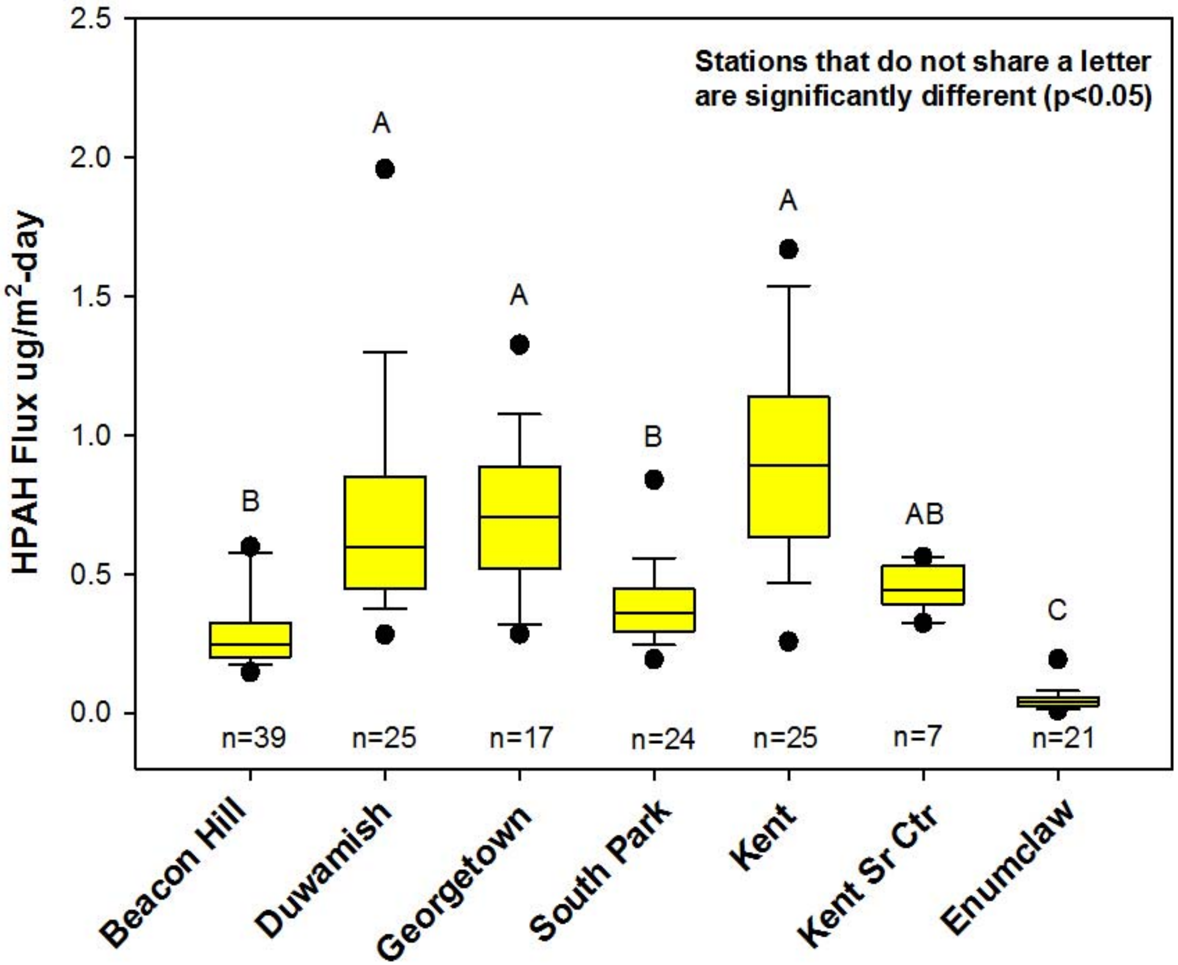
Spatial Trends – Metals: Arsenic



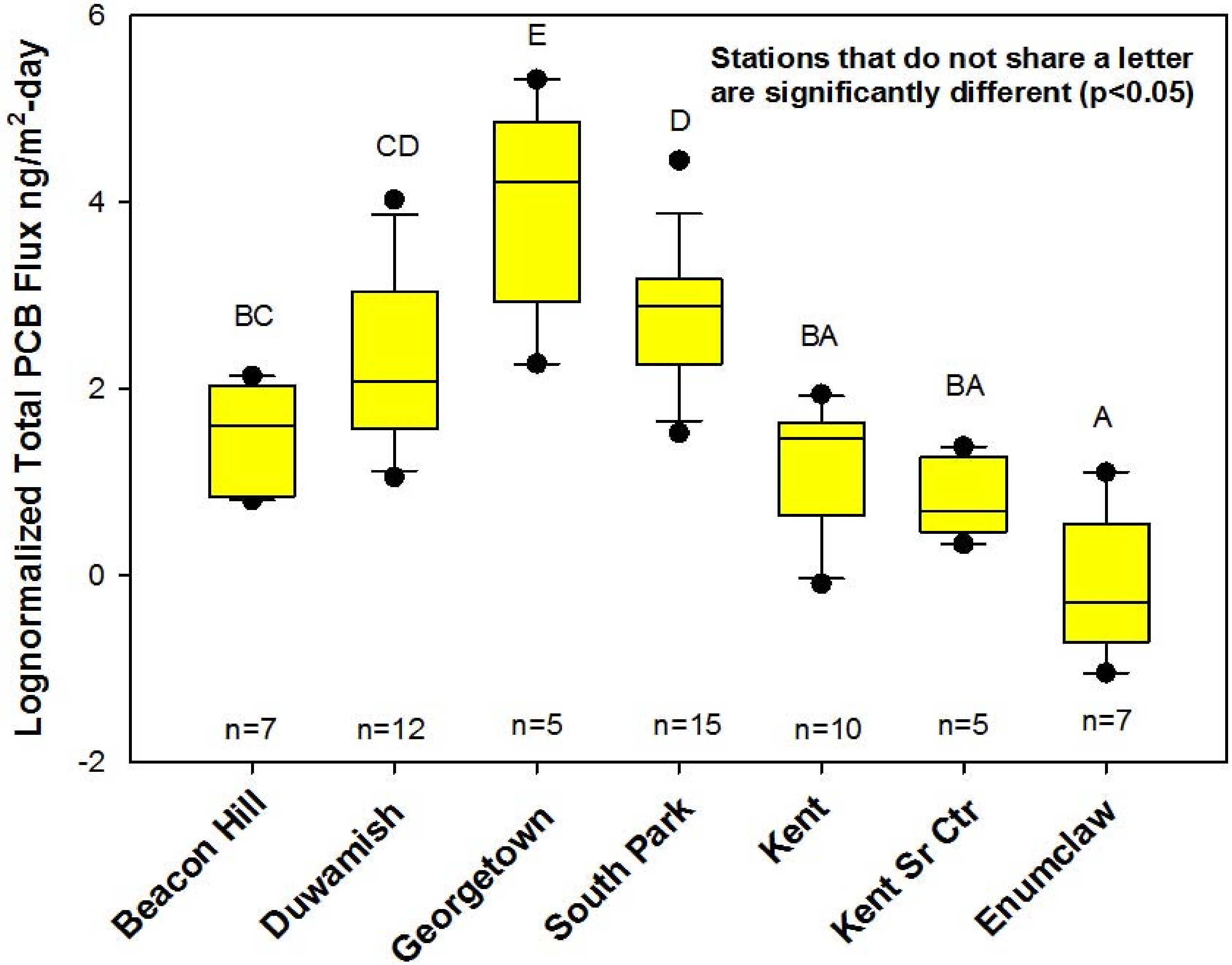
Spatial Trends – Metals: Zinc



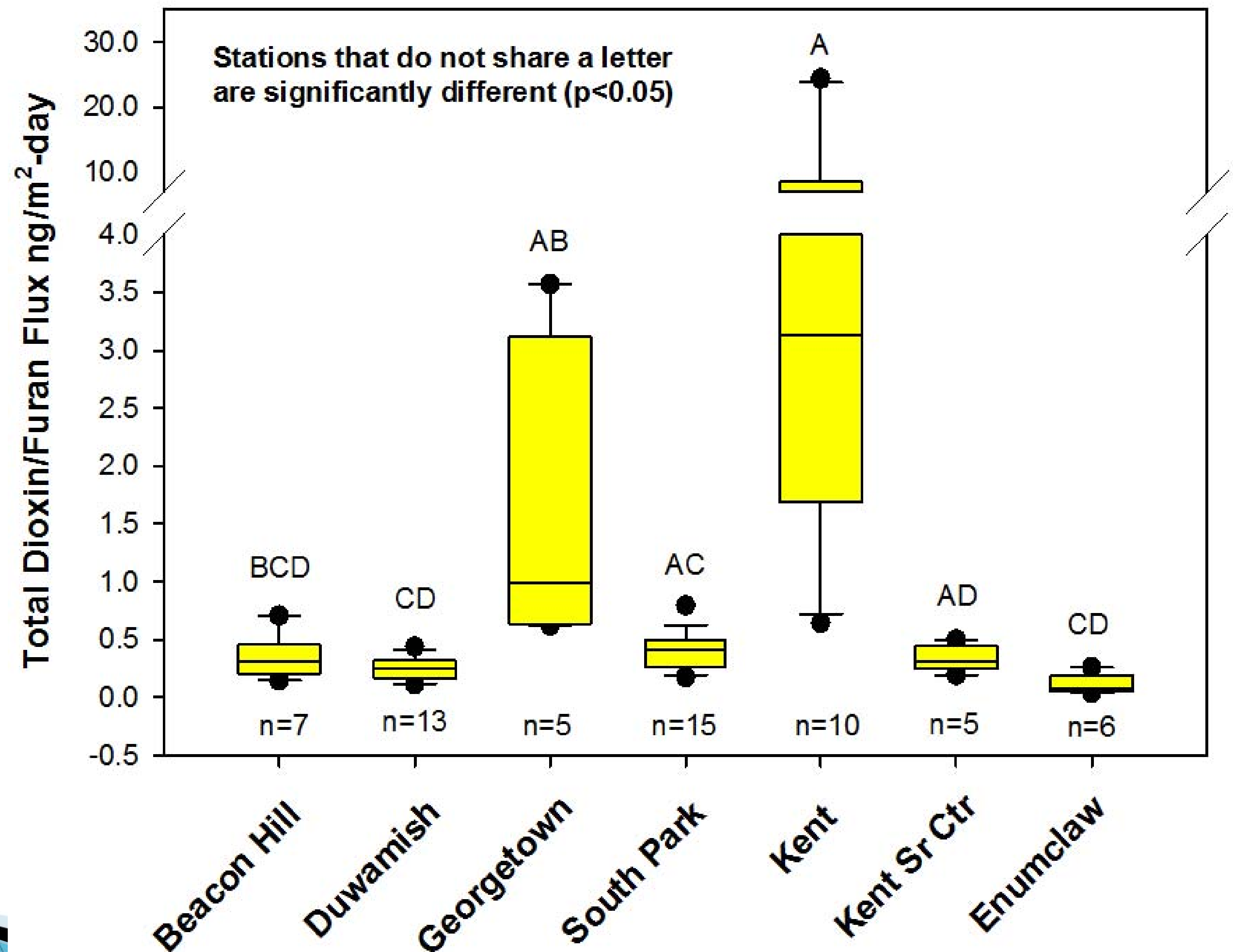
Spatial Trends – HPAHs



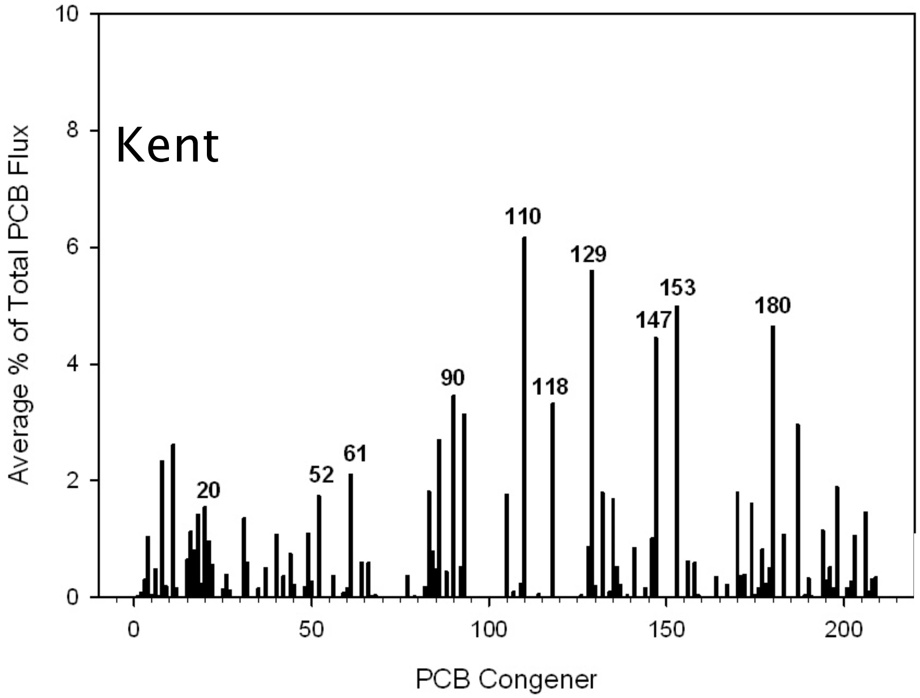
Spatial Trends – Total PCBs



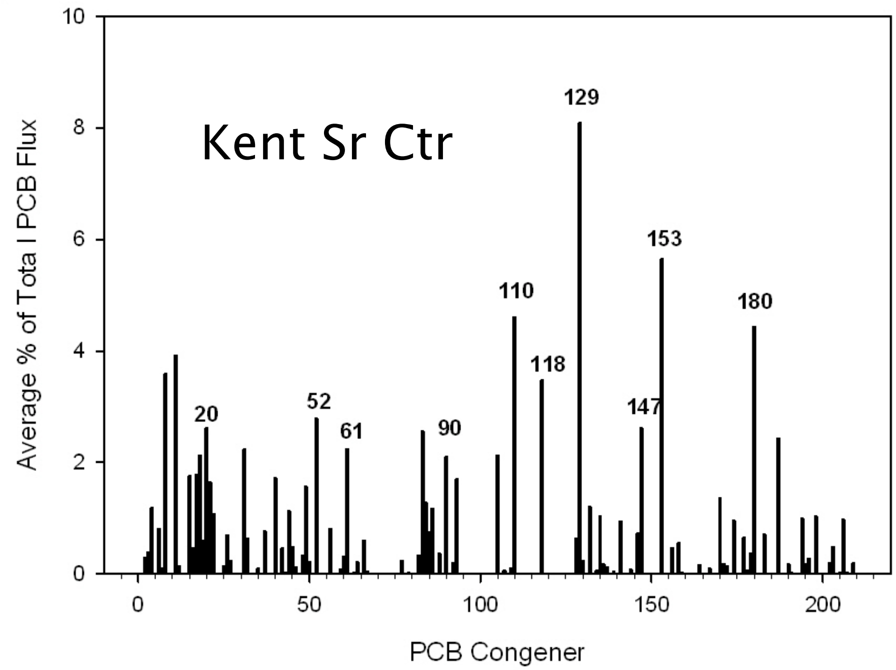
Spatial Trends – Dioxins/Furans



PCB Congeners



- Patterns differ by station
- Different patterns at stations, even 0.3 miles apart
- Indicates local sources are important
- Low chlorinated congeners more important at Enumclaw



Significant Contributing Factors to Flux

	Environmental Variables			
Analyte	Temp	Rain	Wind	PM 2.5
Arsenic			x	x
Cadmium	x		x	x
Chromium			x	x
Copper			x	x
Lead	x		x	x
Mercury	x	x	x	
Nickel	x		x	x
Vanadium	x		x	x
Zinc	x		x	x
HPAHs	x			x
Dioxins/Furans	x			
PCBs	x			x

Air Deposition Findings

- Metals and organics fluxes relate to degree of urbanization.
- Metals and organic fluxes at Duwamish, Georgetown or South Park often highest, Enumclaw lowest.
- Median metals fluxes at Georgetown most often highest of any station; mean PCBs fluxes significantly higher than any other station.

Air Deposition Findings

- High spatial variability seen at small scales, i.e. Kent stations were 0.3 miles apart – very different deposition rates; congener patterns also differ.
- Mean PM 2.5 and wind significant drivers of metals flux; PM 2.5 and temperature are significant drivers of PCBs flux
- PCB congener patterns indicate local sources are important.

Green River Watershed Surface Water Study: Green River and its Major Tributaries

Debra Williston
Carly Greyell
Deb Lester

Study Questions

- How do relative contributions of PCB congeners, PAHs and Arsenic differ between baseflow and storm conditions in the Green River basin?
- What are the relative spatial differences in PCB congeners, PAHs and Arsenic concentrations in the Green River and its major tributaries?



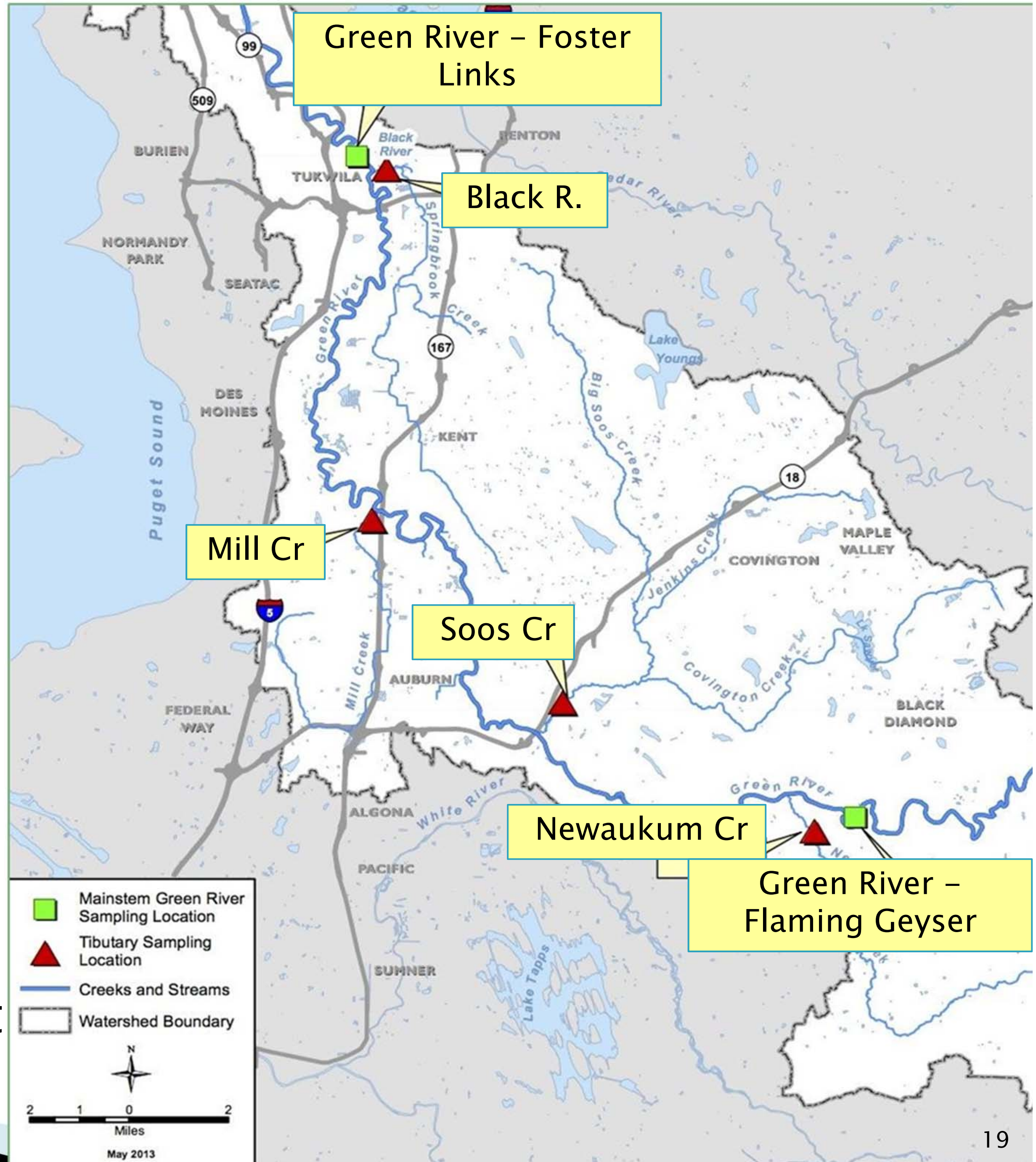
Study Area and 2011/2012 Sampling Locations

Main stem Green River

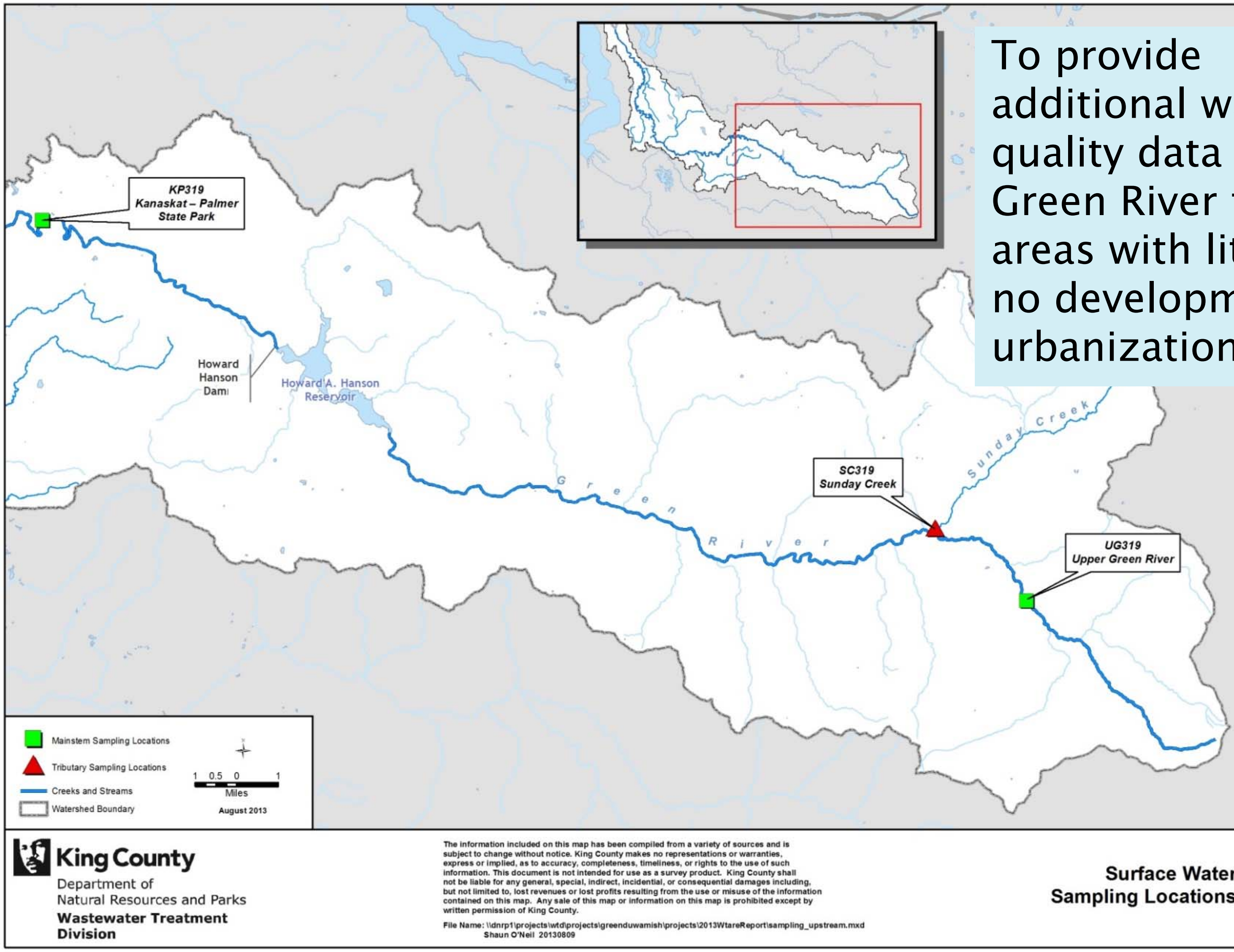
- Flaming Geyser SP
- Foster Links Golf Course

Tributaries

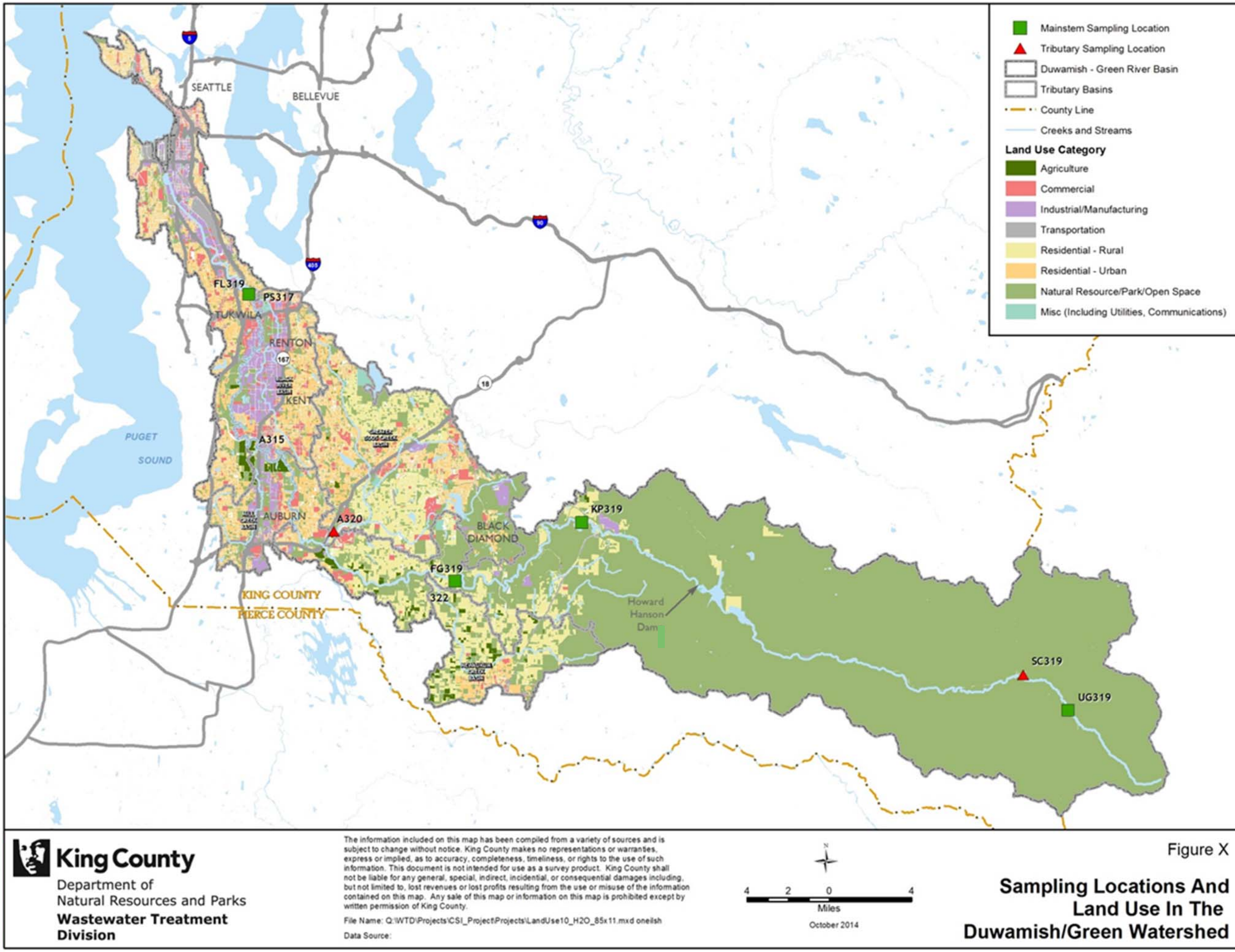
- Soos Creek
- Newaukum Creek
- Mill Creek
- Black River Pump St



2013/2014
Green River Water Sampling Locations



To provide additional water quality data for Green River from areas with little to no development and urbanization


Mainstem Sampling Location
Tributary Sampling Location
Duwamish - Green River Basin
Tributary Basins
County Line
Creeks and Streams
Land Use Category
Agriculture
Commercial
Industrial/Manufacturing
Transportation
Residential - Rural
Residential - Urban
Natural Resource/Park/Open Space
Misc (Including Utilities, Communications)
SEATTLE
BELLEVUE
PUGET
SOUND
FL319
PS317
TUKWILA
RENTON
KENT
A315
AUBURN
A320
BLACK
DIAMOND
KP319
FG319
322
KING COUNTY
PIERCE COUNTY
Howard
Hanson
Dam
SC319
UG319
King County
Department of
Natural Resources and Parks
Wastewater Treatment
Division
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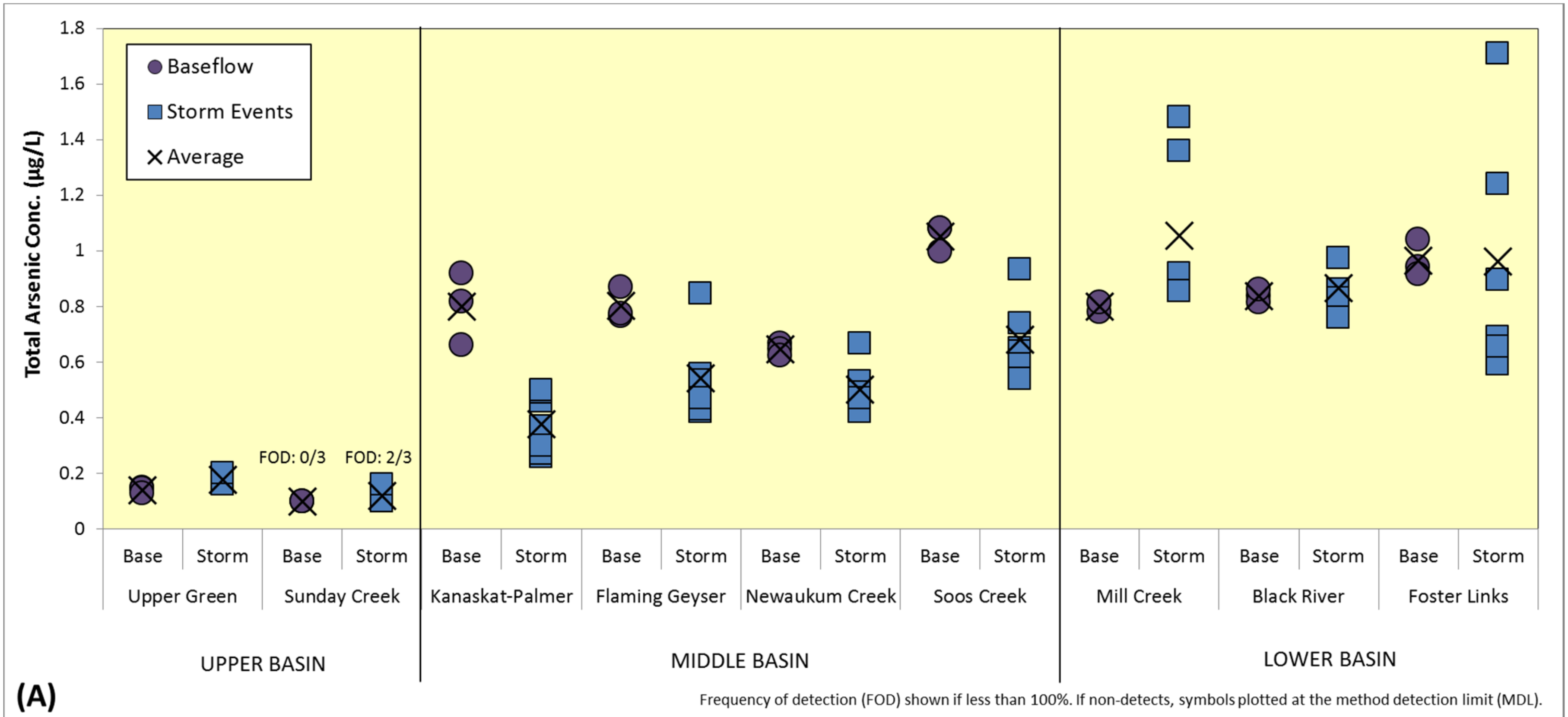
File Name: Q:\WTD\Projects\CSI_Project\Projects\LandUse10_H2O_85x11.mxd oneilsh
Data Source:
4 2 0 4
Miles
October 2014
Figure X
Sampling Locations And
Land Use In The
Duwamish/Green Watershed

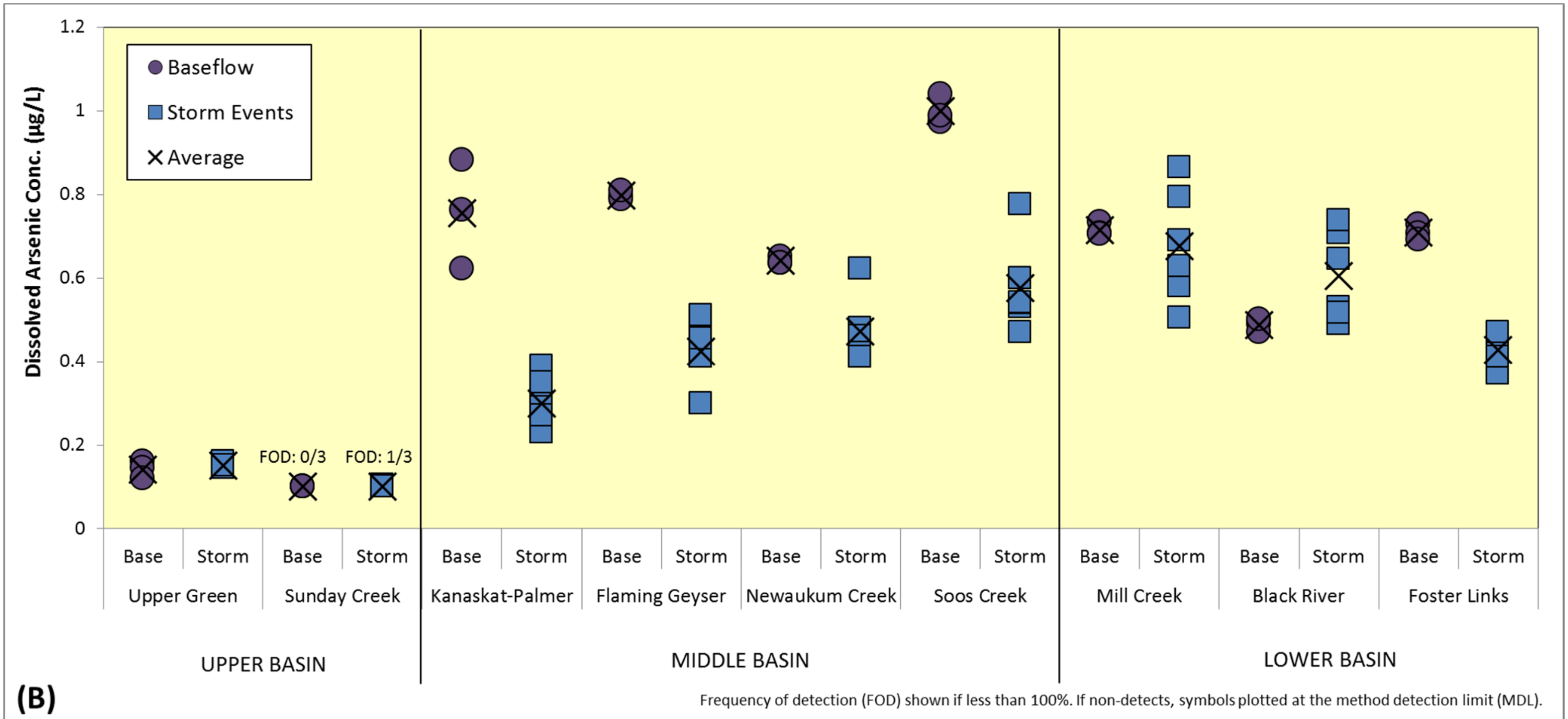
Sampling Methods

- Middle/Lower Green River & Tributary Samples
  - 24-hour composites with ISCO® auto-samplers
  - 3 dry season/baseflow
  - 6 storm/wet season conditions
- Upper Green River Samples
  - 2 hours with 2-L aliquot every 20-30 minutes
  - 3 dry season/baseflow composite grabs
  - 3 storm/wet season conditions composite grabs
- Analysis
  - Samples analyzed for PCB congeners, PAHs, arsenic, total & dissolved organic carbon, total suspended solids

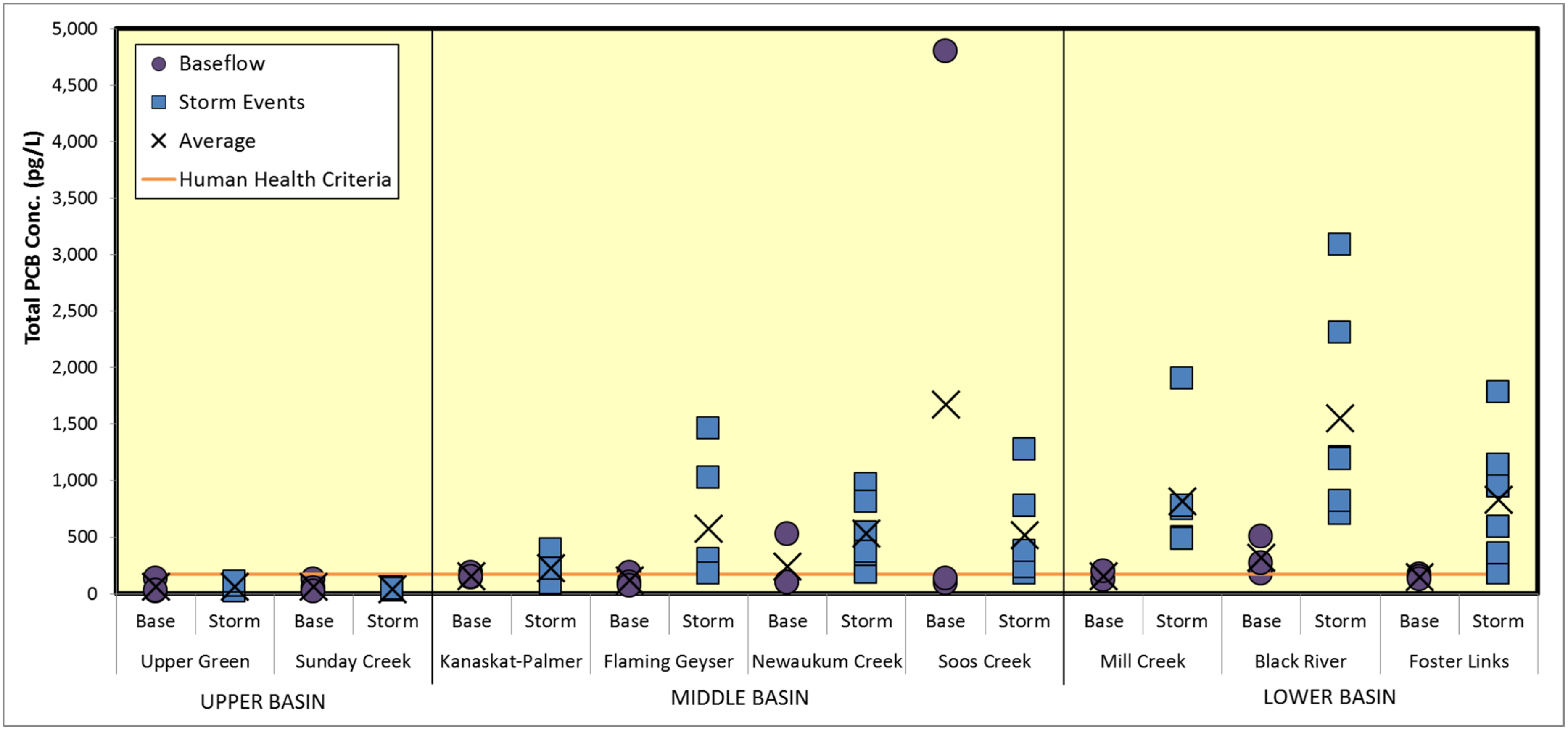
Surface Water Total Arsenic Concentrations



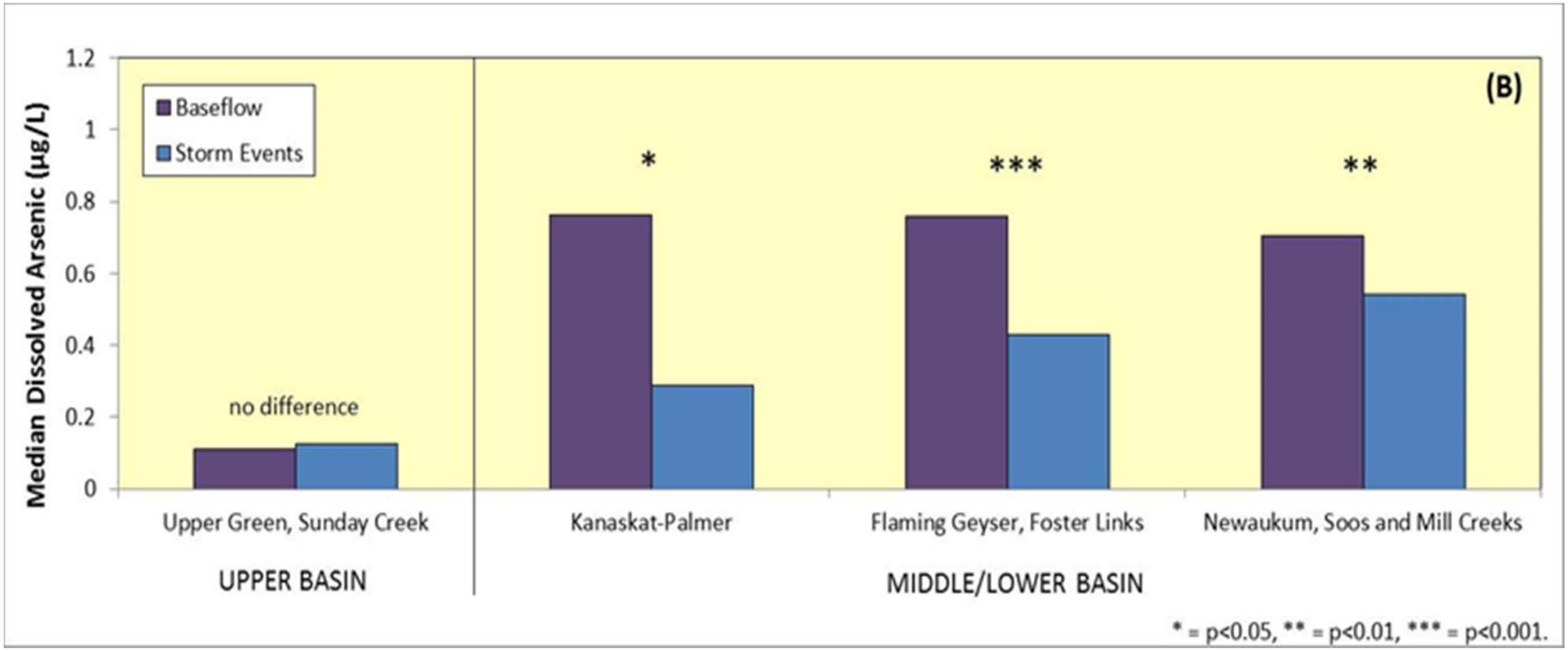
Surface Water Dissolved Arsenic Concentrations



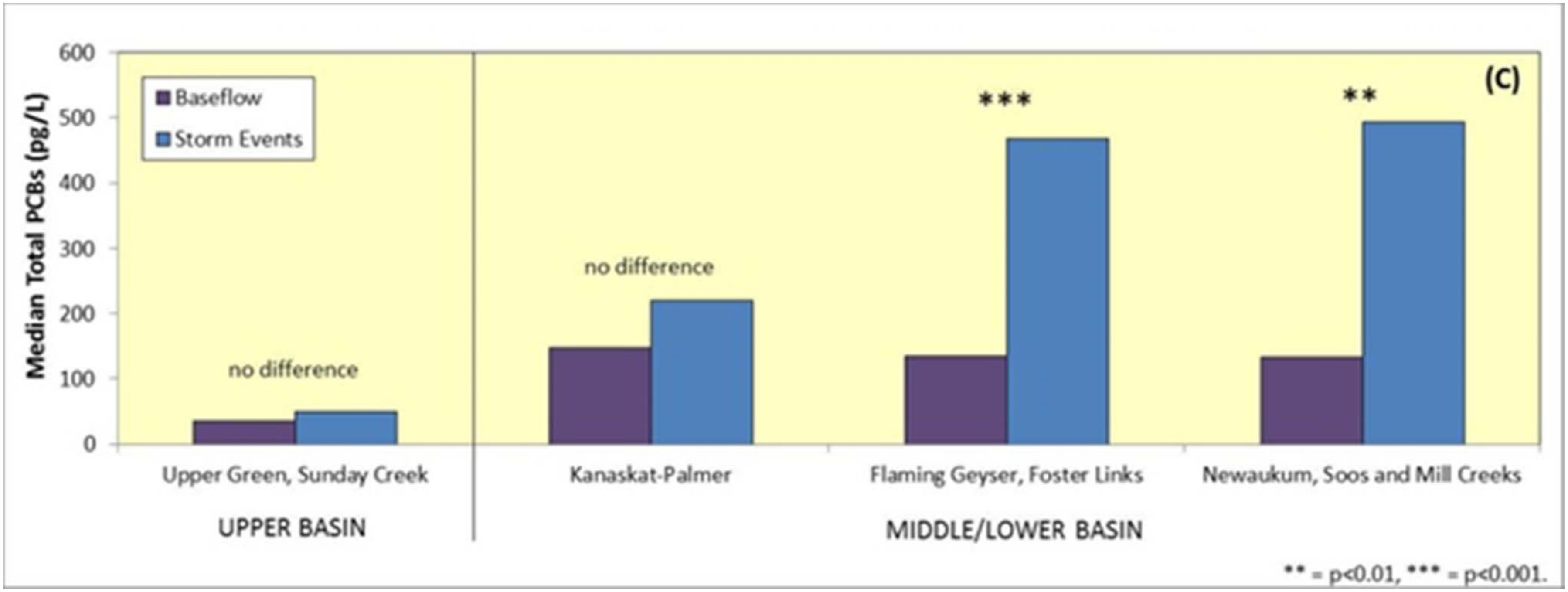
Surface Water Total PCB Concentrations



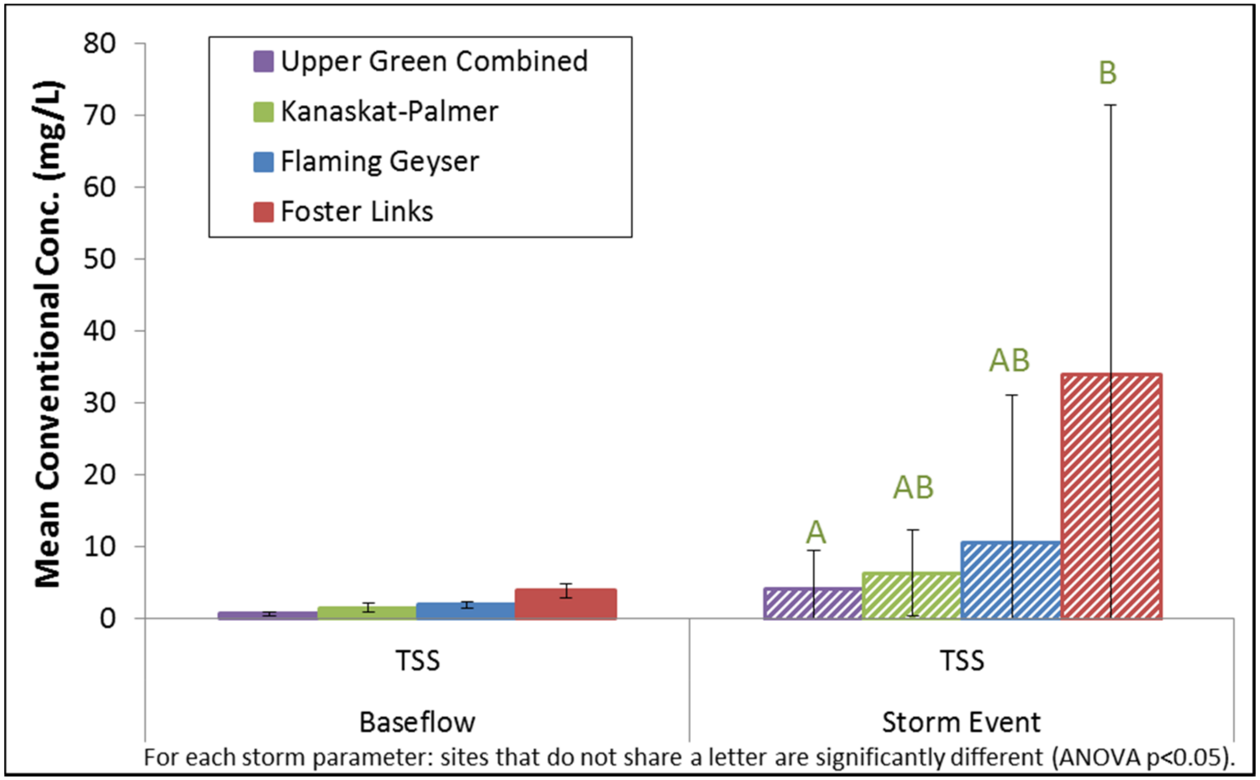
Baseflow vs Storm Events: Dissolved As



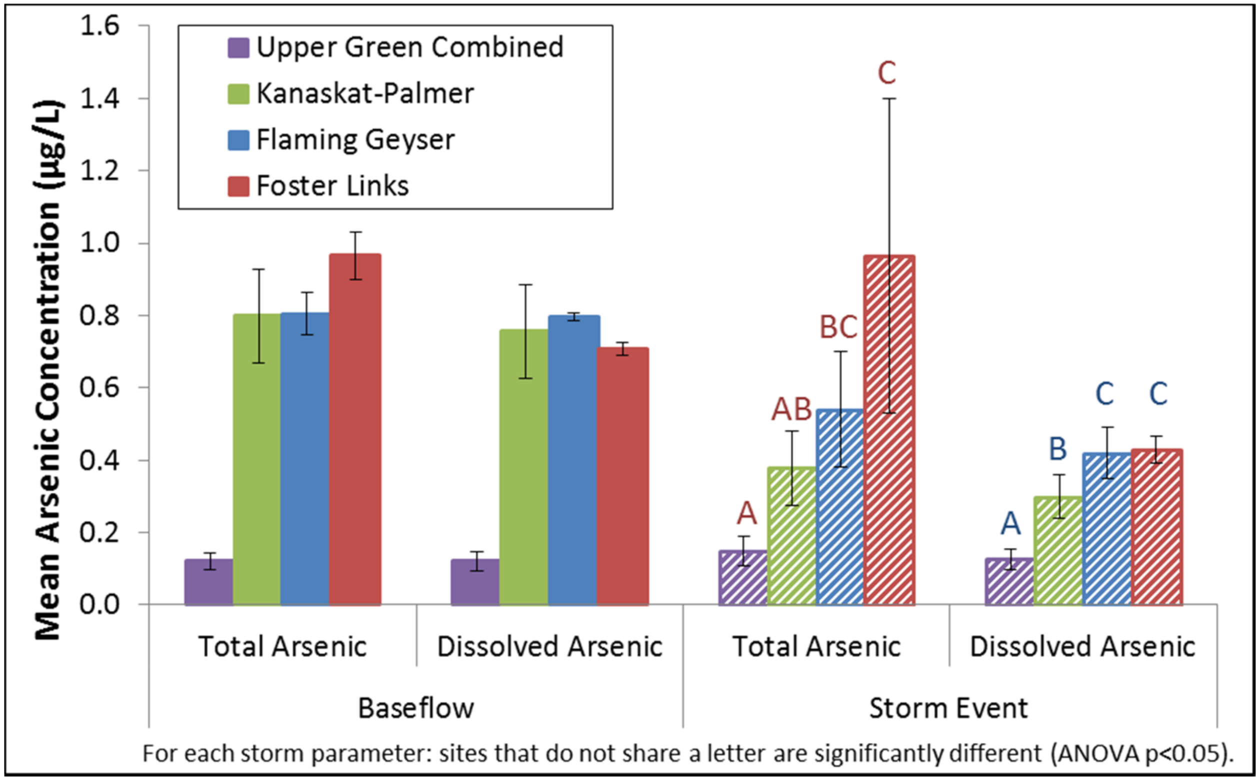
Baseflow vs Storm Events: Total PCBs



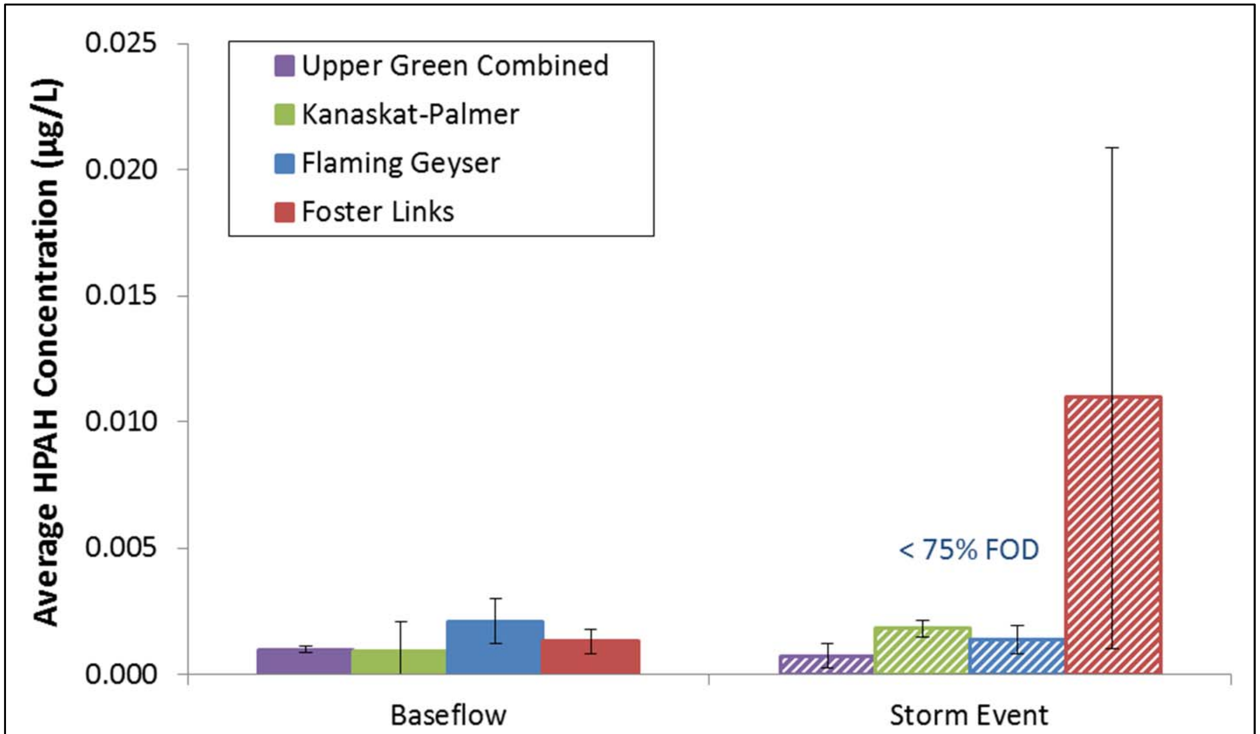
Comparison of Upstream to Downstream– TSS



Comparison of Upstream to Downstream– Arsenic

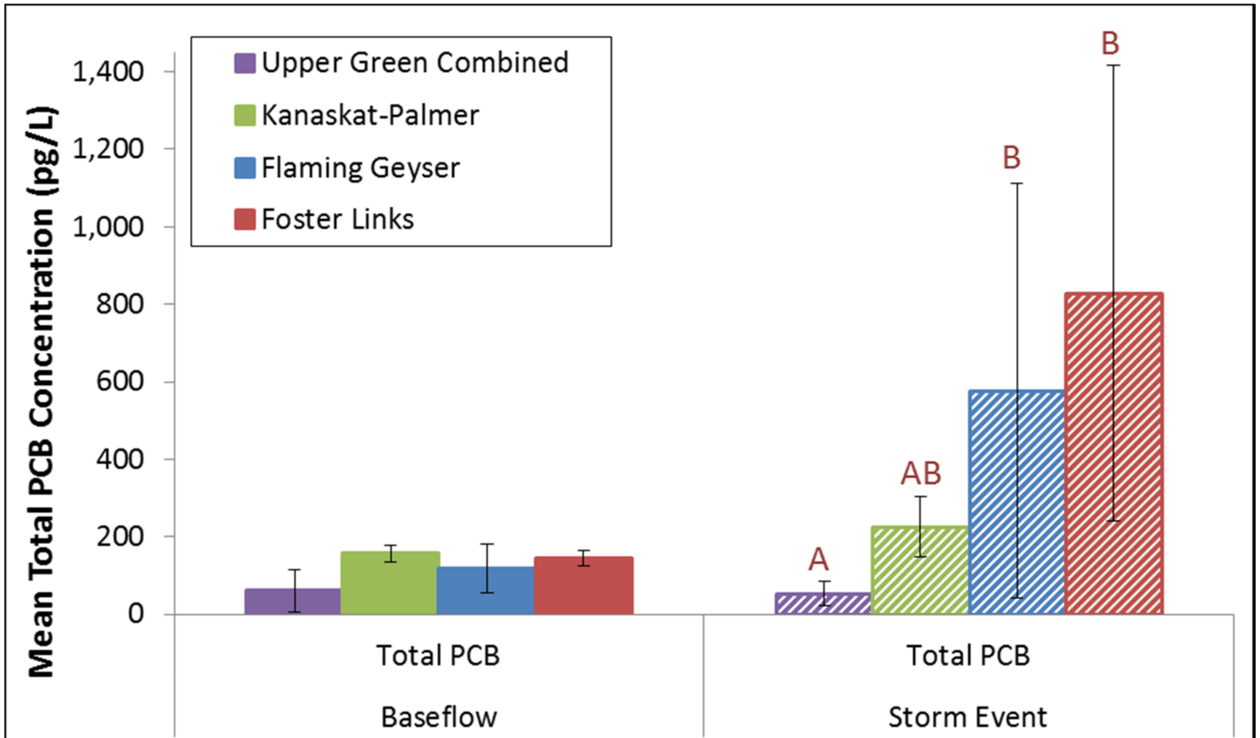


Comparison of Upstream to Downstream– Total HPAHs



Storm statistical differences not considered because frequency of detection was less than 75% at all sites.

Comparison of Upstream to Downstream– Total PCBs



For storm events: sites that do not share a letter are significantly different (ANOVA $p<0.05$).

Note: PCB contamination from autosampler equipment resulting in high bias especially at Kanaskat-Palmer site; degree of bias unknown but Equipment Blank Study underway

Surface Water Summary

- As and PCB Washington State water quality standards (WQS) for the protection of aquatic life:
  - All samples below
- PCB human heath WQS (based on the National Toxics Rule):
  - Upper basin below
  - Tributary sites and Green River within the middle and lower basins exceeded in 41 of 43 storm samples and 8 of 21 baseflow samples
- For some parameters, significant differences in concentration were observed between baseflow and storm event conditions.

Surface Water Summary

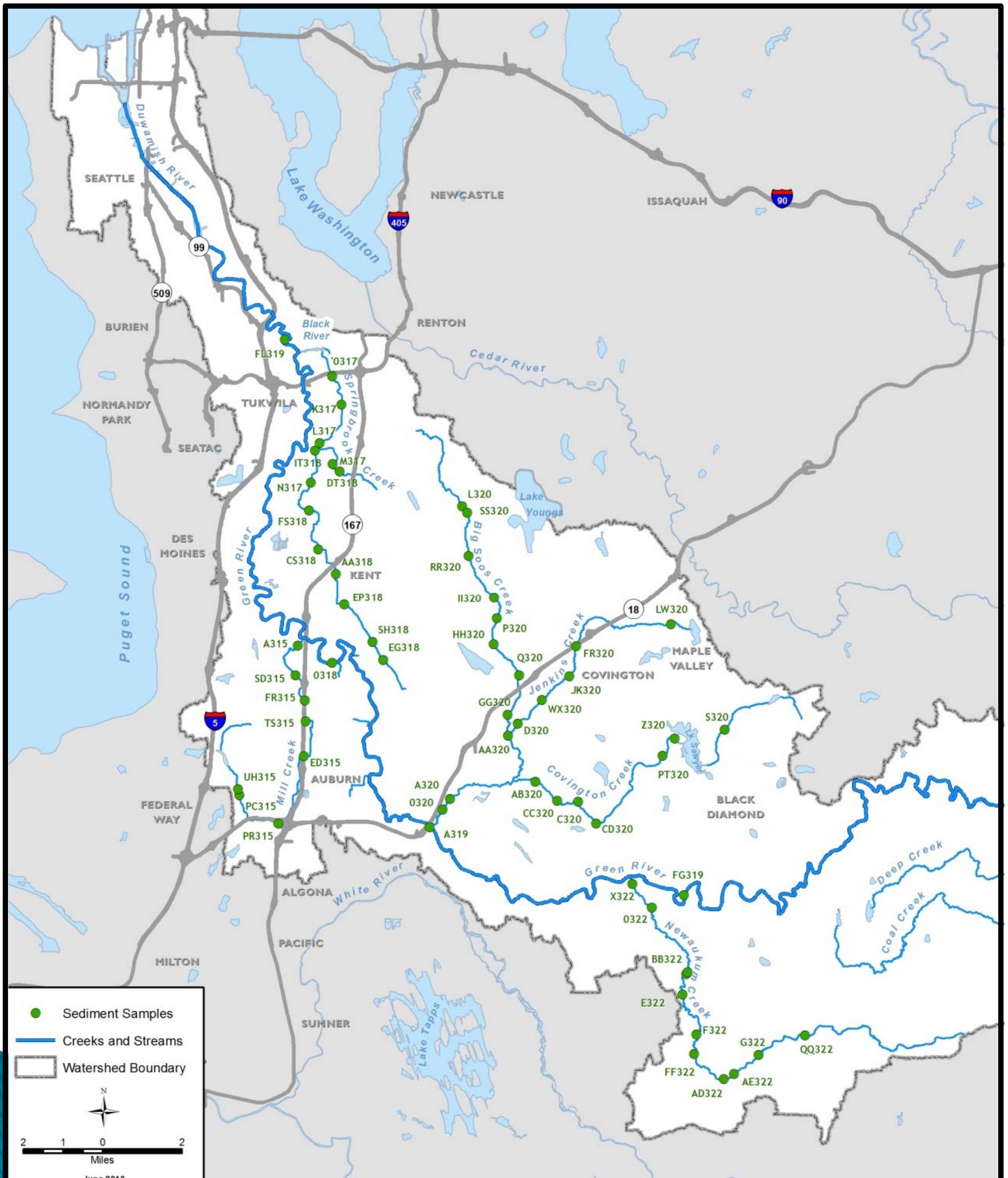
- Significant differences in concentration were also observed between some sampling locations.
- Study findings suggest that stormwater runoff from more developed areas further downstream in the watershed may be contributing to increasing Green River contaminant concentrations.
- Overall, concentrations of arsenic and total PCBs in the Green River (below the Dam) and its tributaries are within the range observed in a study that included the Puyallup and Snohomish watersheds (Ecology 2011).

Contaminants in Green River Basin Sediments

Dean Wilson, Carly Greyell and Debra Williston

Study Goals

- Evaluate sediment quality in the Green River Basin
- Evaluate relative differences in sediment quality between streams
- Better understand upstream contaminant sources to the Lower Duwamish Waterway



Study Area

Sampling Locations

2008-2010

- Soos Creek
- Newaukum Creek
- Springbrook Creek

August 2012

- Mill (Hill) Creek -Auburn
- Mill Creek – Kent
- Jenkins Creek
- Covington Creek
- Green River Mainstem

Sample Collection Methods

- Goal of sampling every mile along tributaries
- Depositional areas targetted
- Composite samples:
  - Tributaries and three Green River Locations
    - 5 hand core grabs
  - Green River – Foster Links
    - 3 Ponar grabs
- Sediment Depth: 5 – 10 cm
- Analyzed for metals/organics/conventionals

Key Findings–Relative Comparisons

- Green River mainstem samples
  - Very few chemicals detected
  - ~ 80% sand, < 1% TOC
- Highest metals:
  - Springbrook Creek
- Highest PCBs and Dioxins:
  - Springbrook Creek, Mill Creek – Kent

Key Findings – Sediment Quality

- All concentrations below Freshwater Benthic CSL
- Relatively few concentrations above Benthic SCO
- Tributaries with most SCO hits:
  - Springbrook Creek, Mill Creek – Kent
- Contaminants with most SCO hits:
  - Arsenic, bis(2-ethylhexyl)phthalate
- AVS/SEM Analysis
  - Where SCO exceeded, AVS/SEM indicate metals may not be bioavailable in almost half the cases

CSL = Cleanup Screening Level

SCO = Sediment Cleanup Objective

AVS/SEM = Ratio of Acid Volatile Sulfides and Simultaneously Extractable Metals

Suspended Solids in the Green River Watershed

Debra Williston
Deb Lester
Carly Greyell

Study Questions

- What are the general chemical characteristics of suspended solids collected over the study period?
- What are initial estimates of the relative contributions of PCBs, PAHs, dioxins/furans and arsenic to the Lower Duwamish Waterway?
  - Sediment Traps and Filtered Solids
- How do concentrations of PCBs, PAHs, dioxins/furans and arsenic associated with suspended solids differ between locations during dry season/base flow and wet season/storm conditions?
  - Filtered Solids

Suspended Solids–Sediment Traps

Four Collection Periods:

- Oct 2012–Feb 2013
- Mar – May 2013
- June – Sept 2013
- Oct 2013 – Jan 2014

Suspended Solids– Filtered Solids

- Stream water pumped through filter housing

- Solids captured on 5 µ polypropylene felt filter, pressure rated to 15 psi

- Targeted Sample Collection for each location
    - One dry baseflow
    - Five storm events/wet season

Suspended Solids in the Green River Watershed

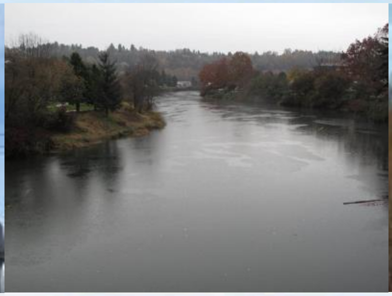
- Sample locations same as 2011/2012 surface water locations
- Samples analyzed for metals, PCBs, dioxins/furans, PAHs, conventionals
- Samples collected Q4 2012 through Q4 2014
- Analytical samples completed Q2 2015
- Data Analysis and Reporting Q2-Q4 2015

Thank You

- Many dedicated King County staff working on projects
  - Wastewater Treatment Division: Jeff Stern on Study Designs
  - Environmental Laboratory & Field Sciences Unit
  - Science Section of Water & Land Resources Division
- Acknowledgement of non-KC staff
  - AXYS Analytical Services
  - Foster Links Golf Course: Curt Chandler and staff
  - South Park Community Center, South Seattle Community College and Puget Sound Clean Air Agency
  - Leidos (formally SAIC): Cory Wilson
  - Ecology: Dan Cargill and John Williamson
- All final reports posted to KC web site

Overview of data gaps and pollutant groupings memo

Green/Duwamish River Watershed



Pollutant Loading Assessment

Technical Advisory Committee Meeting
April 16, 2015

DEPARTMENT OF ECOLOGY
State of Washington

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

TETRA TECH
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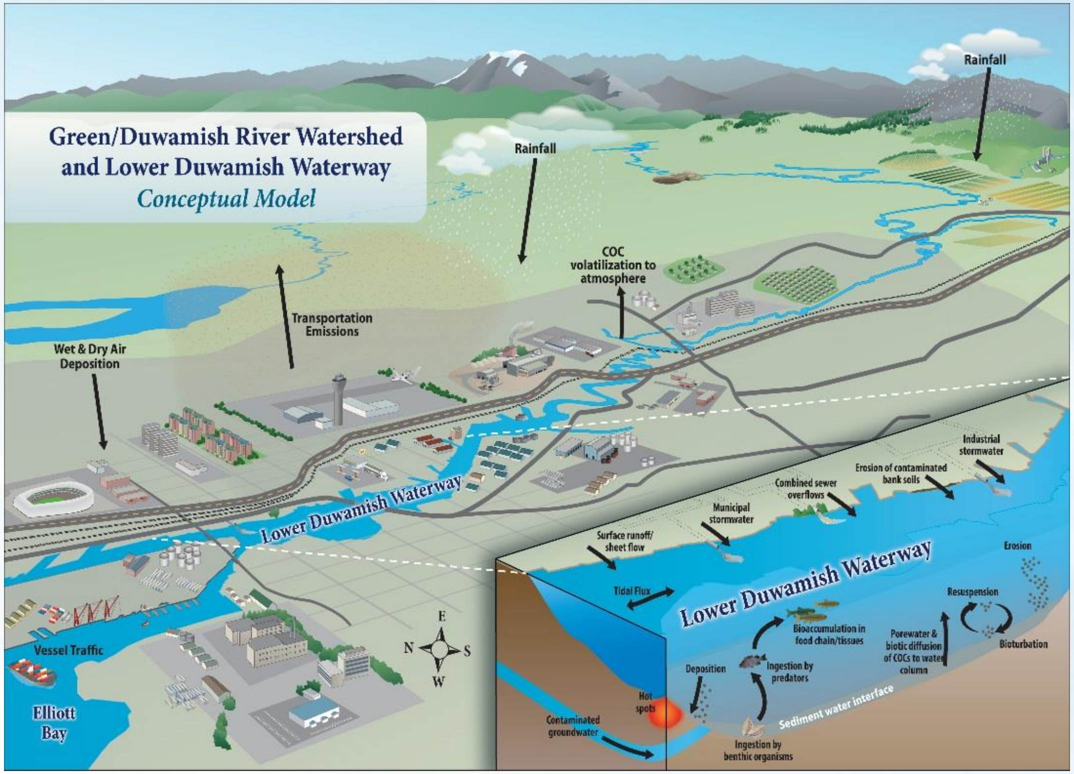
Overview

- ► Review of RI/FS
- ► Addressing data gaps - receiving water model
- ► Pollutant groupings

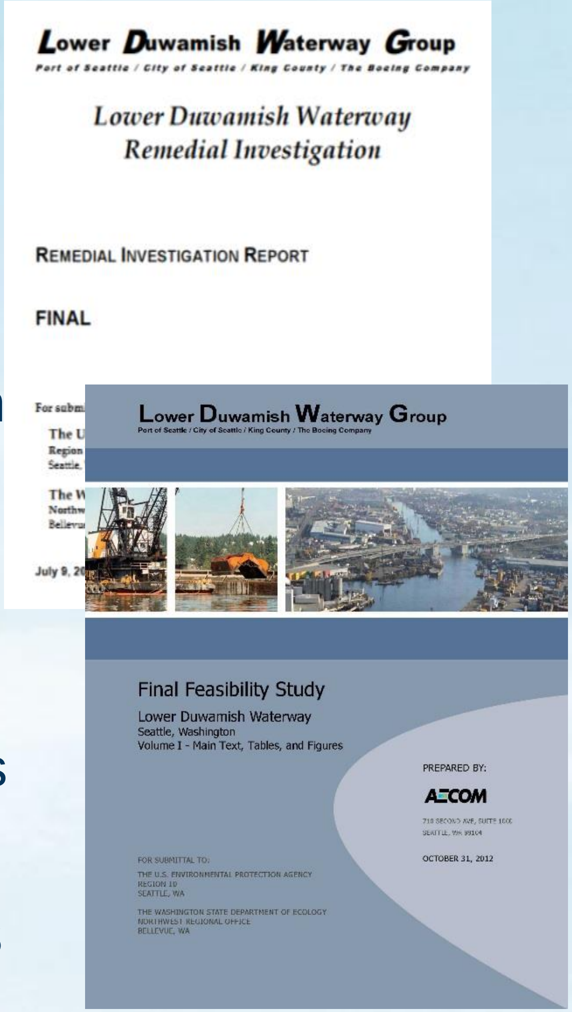


Data gaps/pollutant groupings memo

- Data gaps, strategies to address, and discuss pollutant groupings
- Priority parameters
- Begin with RI/FS information; add data collected since
- More process driven and qualitative
- Information folds into the initial QAPP
- <u>Today</u>
  - discuss some components of this work
  - continue at next TAC

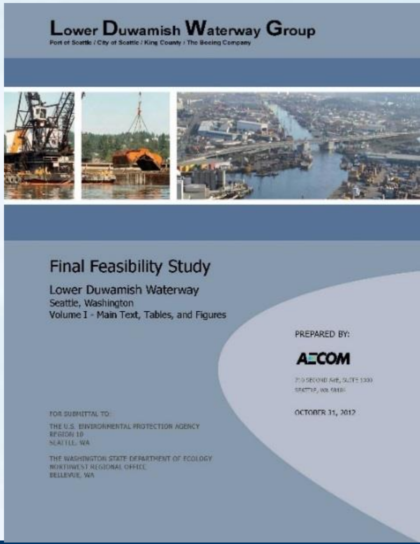
RI/FS provides information basis for PLA

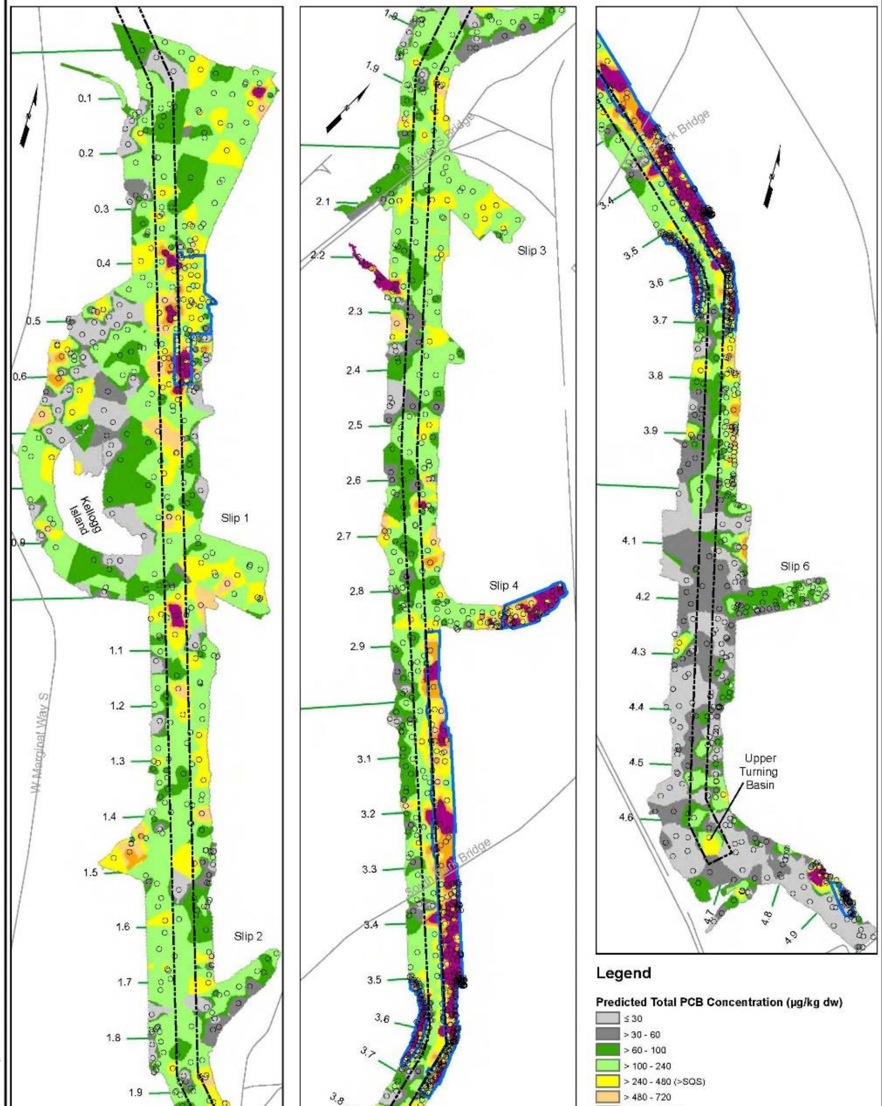
- ► Remedial Investigation
  - Reports on data collected through 2006 and available as of 2008
  - Data restricted to samples after 1990
- ► Feasibility Study
  - Supplements RI adding data collected through early 2010
  - Also reports on the modeling
  - Develops data to support remedial action
- ► RI identified major human health risk drivers: PCBs, arsenic, cPAHs, & dioxins/furans
- ► RI identified 41 major ecological risk drivers, including PCBs, arsenic, & PAHs



Feasibility Study

- ► Developed detailed interpolated maps of COC conc. in sediment
- ► Summarized info on source characterization (through 2010)
- ► Developed detailed flow and sediment transport model (STM)
- ► Bed Composition Model (BCM) modeling focused on risk of recontamination of sediment by ongoing sources of sorbed COCs
- ► Used to predict future sediment conc.
  - ▪ simulates the transport of sediment & infers transport of COCs based on movement of sediment
- ► Food web model - bioaccumulation





Legend

Predicted Total PCB Concentration (µg/kg dw)

- ≤ 30
- > 30 - 60
- > 60 - 100
- > 100 - 240
- > 240 - 480 (>SQS)
- > 480 - 720
- > 720 - 1,300
- > 1,300 (>CSL)

PCB Sample Location

Road
Navigation Channel
River Mile Marker
Early Action Area

Notes:
1. Grid interpolated using the following parameters: Power 5, nearest neighbors 10/1, search radius 150x150 ft.
2. Sampling dates of the data range from 1991 to 2010.
3. PCB data from FS baseline dataset dated April 28, 2010.
4. SQS value of 240 µg/kg dw based on conversion of 12 mg/kg oc to a dry weight value using 2% TOC.
5. Two outliers (2,900,000 and 230,000 µg/kg dw) at the head of the Trotsky inlet (RM 2.2) were excluded from use in the interpolation.

Feet
0 200 400 800

AECOM Lower Duwamish Waterway Group

Lower Duwamish Waterway
Final Feasibility Study
60150279-14.34

Interpolated Total PCB Distribution in Surface Sediment

DATE: 10/31/12 | DWRN:MVI/sea | Revision: 0 | **FIGURE 2-13**

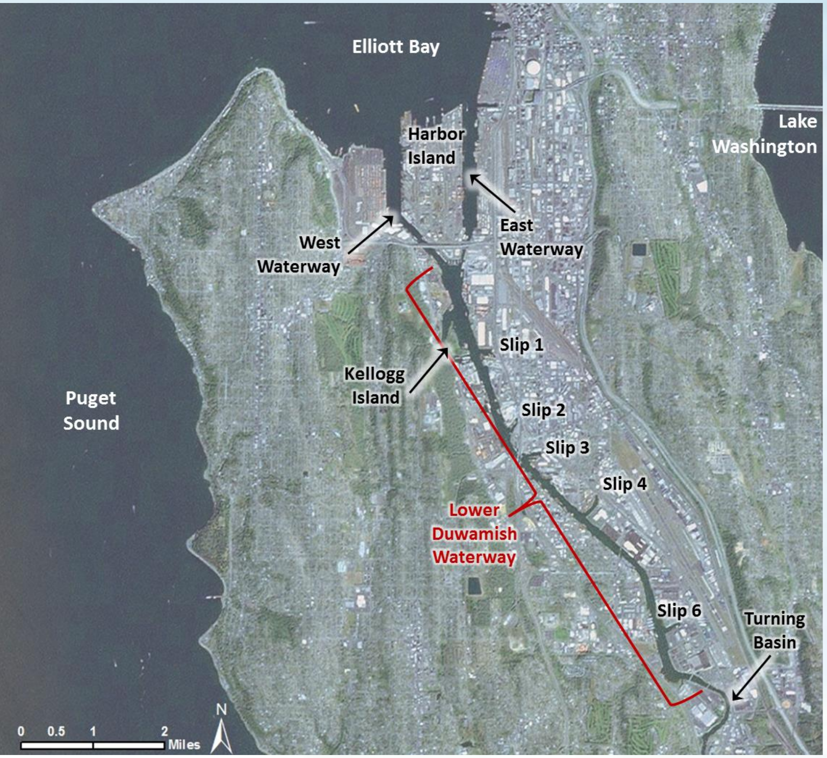
Some conclusions based on the RI/FS

- ► Primary risk drivers associated with legacy releases of chemicals from diverse sources, resulting in large storages of COCs in LDW sediment.
  - High degree of heterogeneity in sediment concentrations
- ► Good characterization of COCs in sediment
- ► Incomplete information on upstream watershed sources
- ► Water column data limited
  - both total & sediment-sorbed
- ► Storm sewer & combined sewer sources to LDW
  - heterogeneous and incompletely characterized (as of early 2010)
- ► Multiple sources and highly variable conc.
  - A challenge for watershed-scale modeling

PLA Focus

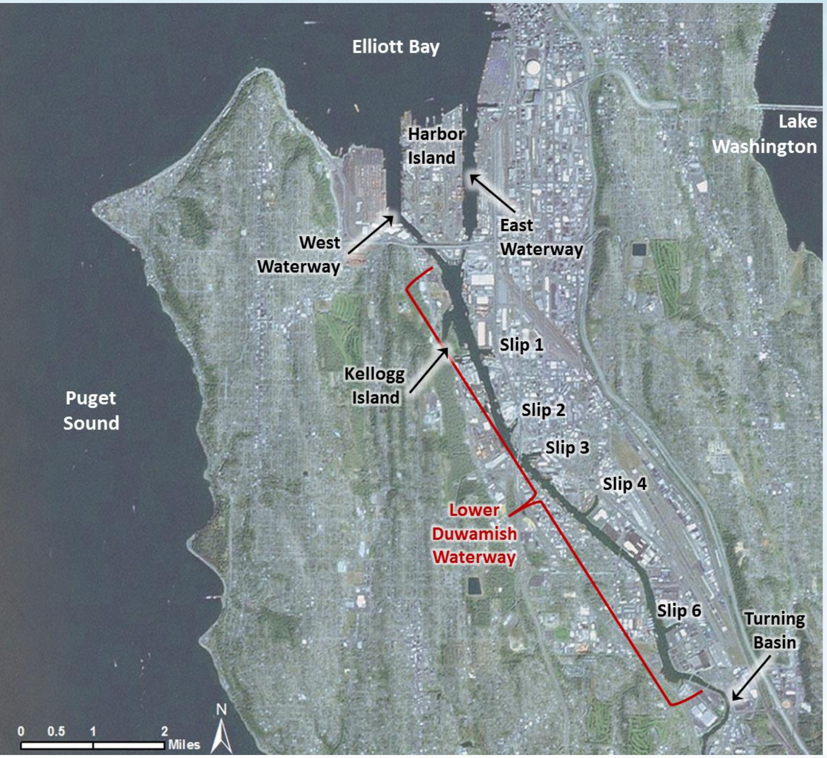
- Water Column
  - Limited water column data associated with RI/FS addressed in part by additional sampling since
  - RI/FS modeling assumptions
    - Did not model COCs in water column (except as source)
    - BCM assumes contaminants strongly bound & no mass loss to degradation or volatilization
    - No transfer between sed & water
- Incoming Sediment/Contaminants
  - RI/FS cites major source of uncertainty in model predictions as incoming sediment, the contaminant concentration of those sediments, and a number of loss processes

RI/FS is data rich for…



- ► Modeled parameters generally well characterized in sediment and tissue
  - PCBs
  - Arsenic
  - cPAHs
  - dioxins/furans
- ► Arsenic - Dissolved and total available for water samples

Data gaps for LDW based on RI/FS



- PCBs –Water column data; Porewater samples
- PAHs –Water column data; Porewater samples
- BEHP –Water column data; Porewater samples
- Metals – Human health risk assessment concluded was not a risk driver
  - Small amt of water column data; methylated mercury?
- Limited information on watershed inputs – Green River
- Limited atmospheric deposition data

New Sources of Data to Address Gaps

- USGS monitoring, Duwamish River at Tukwila 2013
  - Water Column
  - Suspended Sediment
  - Bed Sediment
  - All COCs of interest
- ACOE Study
  - PCBs
  - Ongoing
  - Timeline for results?

USGS science for a changing world

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New Sources of Data to Address Gaps

- King County (2013)
  - Atmospheric Deposition Study
  - 2011-2012
  - 5 stations, multiple parameters
- King County (2014a)
  - *Sediment Quality in the Green River Watershed*
  - metals incl. mercury, PAH, PCB (as Aroclors), dioxin/furan, phthalates, others;
  - 4 locations in 2012; 3 in 2008-2010

King County

New Sources of Data to Address Gaps

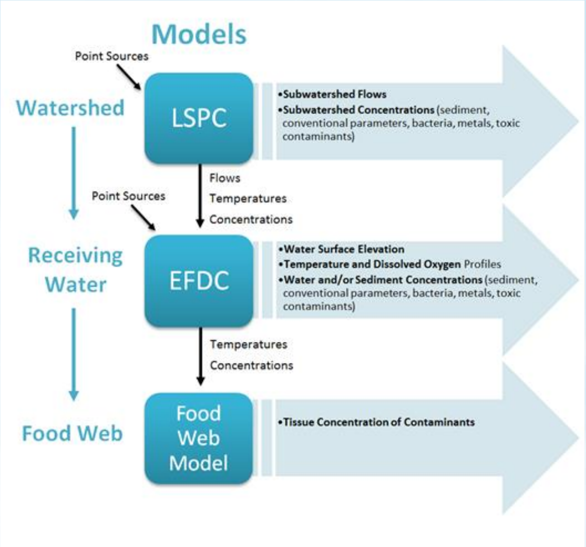
- King County (2014b)
  - *LDW Source Control - Green River Watershed Surface Water Data Report*
    - arsenic, PAHs and PCBs (as congeners) collected in 2011 and 2012
    - Four major tribs, two main stem
- King County (2015)
  - Lower Duwamish Waterway Source Control: Upper and Middle Green River Surface Water Data Report
    - surface water concentrations of arsenic, PAHs and PCBs (as congeners) in samples collected in 2013 and 2014
    - 3 stations - two above Howard Hanson Dam; and one below Dam

New Sources of Data to Address Gaps

- Additional ongoing studies
  - King County Green River/Tribs suspended sediment (sediment traps and filtered solids) data
    - report is not yet published
  - Others

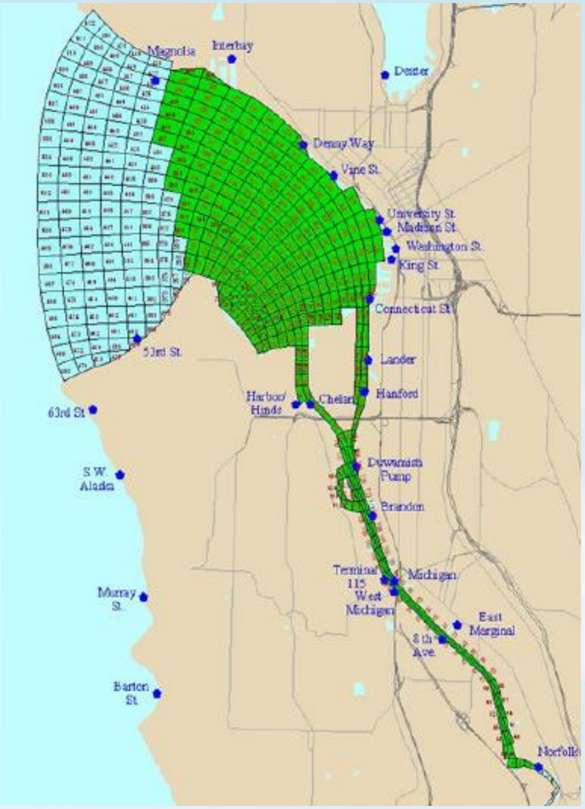
Revisit of Data Needed to Support Model Development

- Three models for Duwamish/Green River
  - Watershed, receiving water, and food web
- Modeled processes
  - Hydrology, hydrodynamics, thermodynamics
  - Sediment transport
  - Toxicant fate and transport
- Four types of data
  - Background data – model configuration
  - Boundary conditions – model configuration
  - Kinetic processes (e.g., partitioning)
  - Data to support model calibration and validation



Data to Support EFDC Configuration and Calibration

- ► Background data
  - bathymetry, and hydraulic structures
- ► Boundary forcing
  - meteorological, inflows, watershed model loading, tide
- ► Calibration/validation data
  - water surface elevation, salinity, temperature, water quality & sediment quality
- ► Point sources
  - direct to EFDC domain



Background Information for Receiving Water Model

- Initial conditions in the LDW
  - Existing sediment and toxics fate and transport modeling
  - LDW dynamics
  - Initial sediment and contaminant levels will have significant impact on the future sediment and contaminant levels
  - Gaps can be filled with historical data and previous model results
  - Historical sediment data from multiple stations are available for all the selected parameters

Boundary Conditions for Receiving Water Model

- Upstream boundary conditions
  - Flow and loadings of sediment and contaminants from Green River
- Lateral boundary conditions
  - Tributary and lateral inflows below the upstream end of EFDC
  - Stormwater runoff and loadings
  - Flow and loadings from CSOs
- Downstream boundary conditions
  - Tide and concentrations of sediment and contaminants in Elliott Bay

General Boundary Condition Data Filling Approaches

- Linear interpolation → short term data gaps
- Monthly average and long-term values → long-term data gaps
- Regression
- Proven algorithms
- Derivations from other parameters
- Patching data from other stations
- Low concentration assumptions
- Existing models to fill gaps
- LSPC model → gaps for pollutant loadings
- Calibration methods

Boundary Condition Data Filling Approaches for EFDC

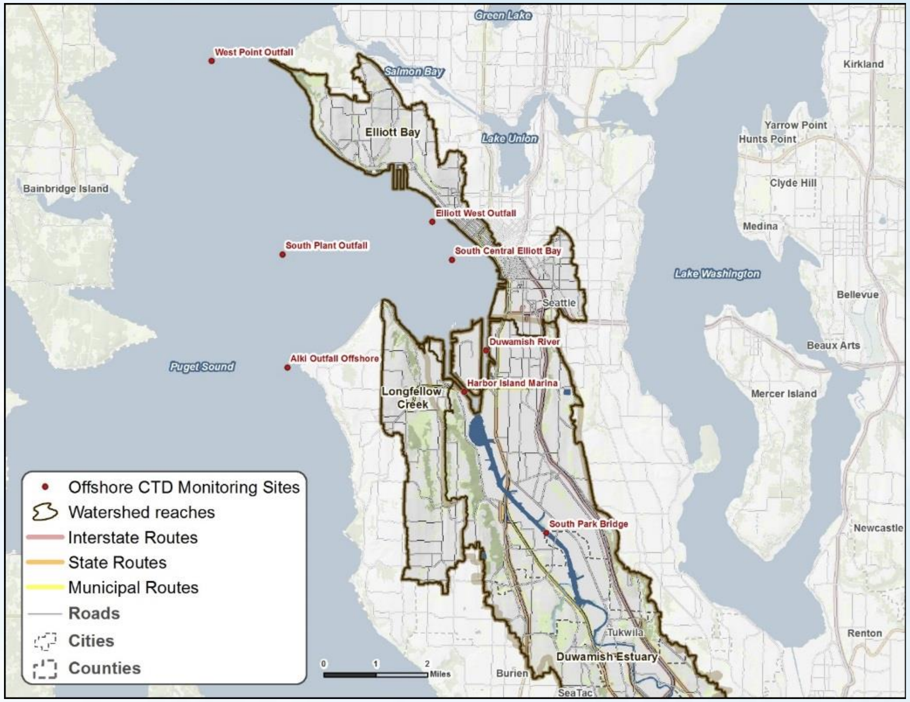
- Upstream boundary conditions
  - LSPC model

Boundary Condition Data Filling Approaches for EFDC

- Lateral boundary conditions
  - LSPC model for the lateral inputs below the EFDC upstream boundary location
  - LSPC model for the stormwater input surrounding the Duwamish Estuary
  - Combination of CSO data and model
    - Potential approaches: average concentrations of monitoring data

Boundary Condition Data Filling Approaches for EFDC

- ► Downstream boundary conditions in Elliott Bay
  - Turbidity to represent suspended sediment
  - Assuming low level of selected parameters
  - New data collection
  - Existing model



Data Gaps: Kinetics in Receiving Water Model

- ► Limited paired sediment-porewater data and suspended solids – dissolved data for organics
  - Partitioning behavior is typically site-specific, depends on sorbents
- ► No measurements of sediment – water fluxes
- ► Limited information on degradation rates
- ► Lack of methylmercury data
- ❖ Kinetic rates can be estimated from literature, but site-specific information would be preferable

Data Gaps for Calibration

- Data and model calibration
- Data gaps
- Knowledge gaps
- Purpose of model calibration and validation

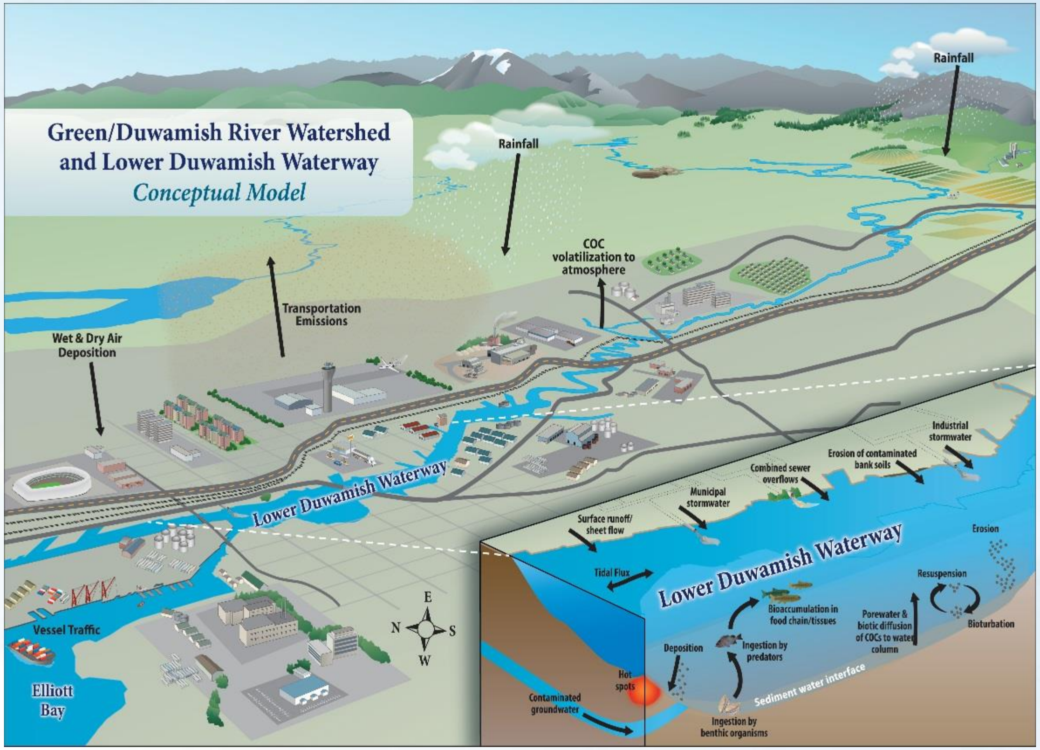
Filling Knowledge Gaps: Receiving Water Model

- Multiple ways to identify the rates and coefficients
  - In-situ measurement or lab experiments
  - Variations of rates and coefficients can be caused by environmental conditions.
  - Explore fundamental mechanisms during calibration to reduce uncertainties
  - Maximal use of data: time series, spatial trends, statistics.
  - Literature values.
  - Apply sensitivity analysis
  - Apply uncertainty analysis

Questions and Discussion

Pollutant Groupings

- ► Preliminary selection of pollutants
- ► Characteristics, how they behave in the environment
- ► Implications for data gaps



Proposed Contaminants of Concern

- PCBs: 209 congeners in 10 homolog groups (# of substituted chlorine atoms)
- Dioxin: 2,3,7,8-TCDD only
- cPAHs (7 selected)
- DEHP (bis-2EH-phthalate)
- Mercury
- Arsenic
- Copper
- Zinc

Lipophilic non-polar organics

Low solubility semi-volatile

More soluble organic

Metal, most toxic organic

Metal, most toxic inorganic

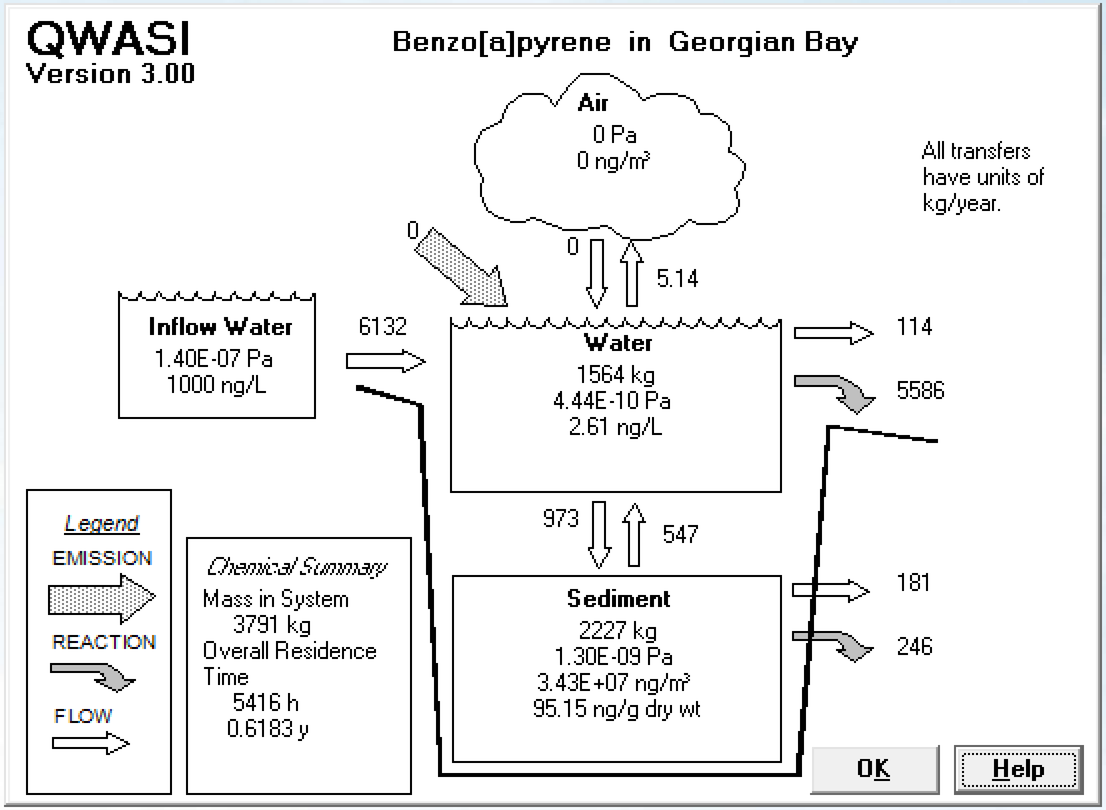
Metal ions

Pollutant Behavior

- Non-polar organics
  - Solubility/volatility (Henry's Law constant)
  - Affinity to sorb to organic carbon (partition coefficient)
  - Rates of exchange from sediment
  - Microbial degradation rates
- Fugacity approach, based on chemical equilibrium concepts, useful for understanding organic compounds – Examples (NOT from LDW) follow

Example Fugacity Model

- Given chemical constants, where does a pollutant reside?
- Important for analysis of gaps in stores and rates



Fugacity Example

- ► EQD example application
- ► Given chemical characteristics and a rate of discharge (1000 kg/h to water in this case), where does the chemical end up?

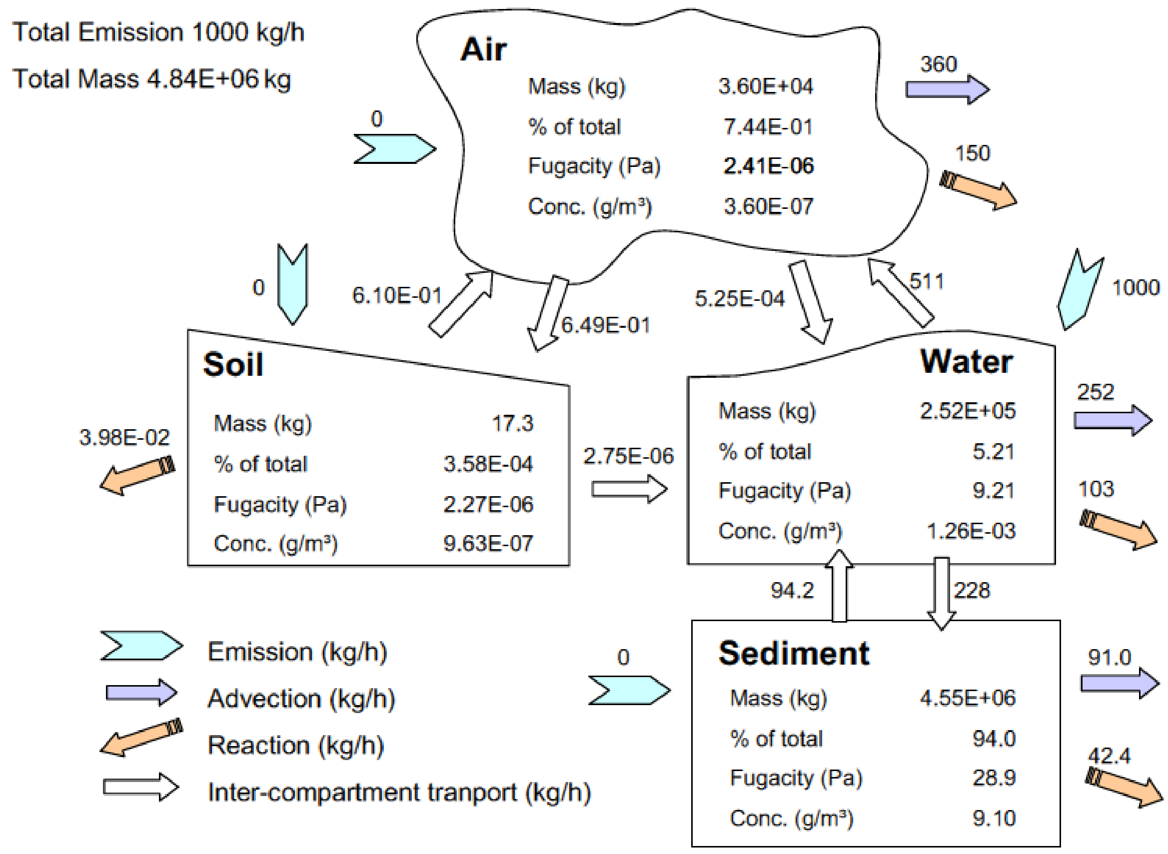


Fig. 3. Level III results for 100% emission of D5 to water.

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An updated state of the science EQC model for evaluating chemical fate in the environment: Application to D5 (decamethylcyclopentasiloxane)

Lauren Hughes [a], Don Mackay [a,*], David E. Powell [b], Jaeshin Kim [b]

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[b] Dow Corning Corporation, Health and Environmental Science, Midland, MI 48686, USA

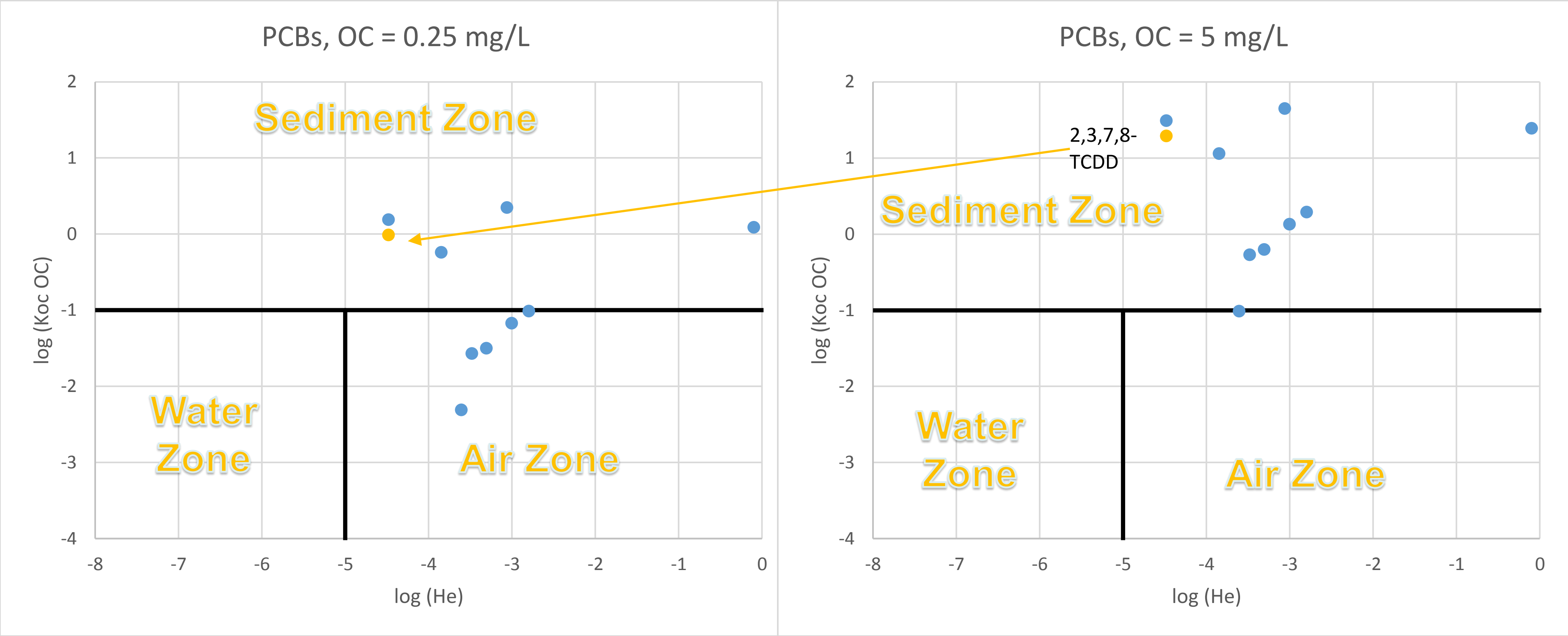
Fugacity Models

- ► Useful scoping tool
- ► Potential problems arise:
  - Equilibrium assumptions often not valid
  - For both sorption and Henry’s Law coefficients there is lots of literature but little agreement: may need site-specific calibration data.
  - Three-phase sorption may play a significant role (sorption to DOC)
  - Temporal variability in sorbents (e.g., water column POC and DOC; porewater POC and DOC) is important, but data are sparse

Chapra Models as Guide to Understanding

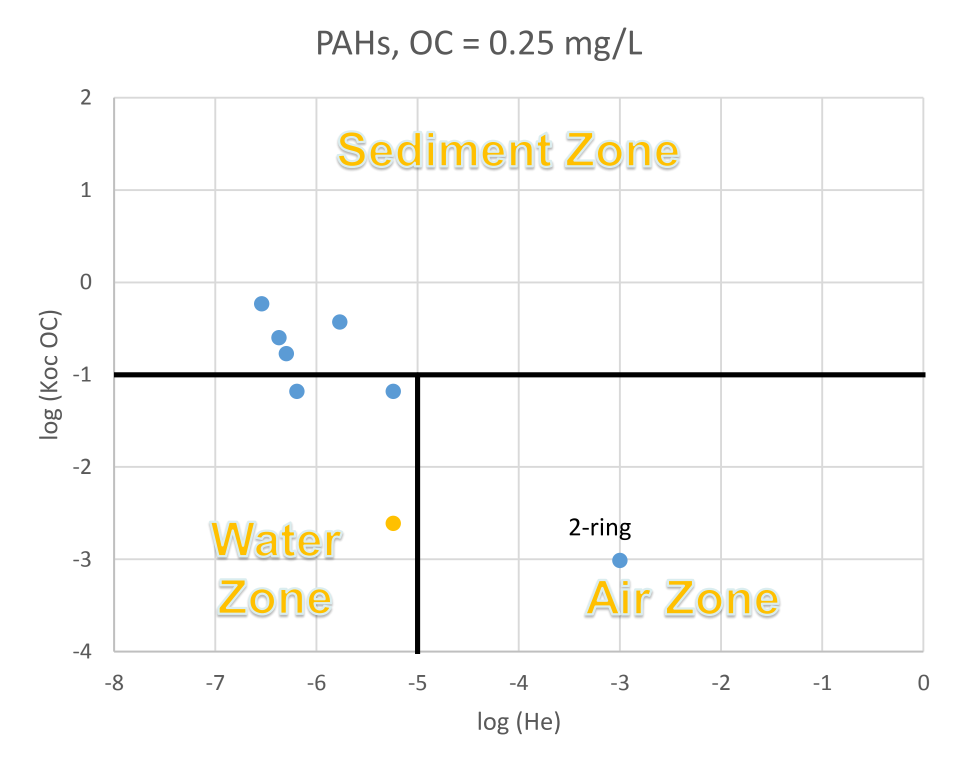
- Note: We have not developed fugacity models for LDW to date
- Simplified approach to understanding available from work of Steve Chapra, “Toxicant-Loading Concept for Organic Contaminants in Lakes” (J. Environ. Eng., 1991, 117:656-677)
- Predicts steady-state distribution of organic pollutants based on sorption and volatilization characteristics
- Produce conceptual map of whether pollutant is predominantly in the sediment zone, the water zone, or the air zone

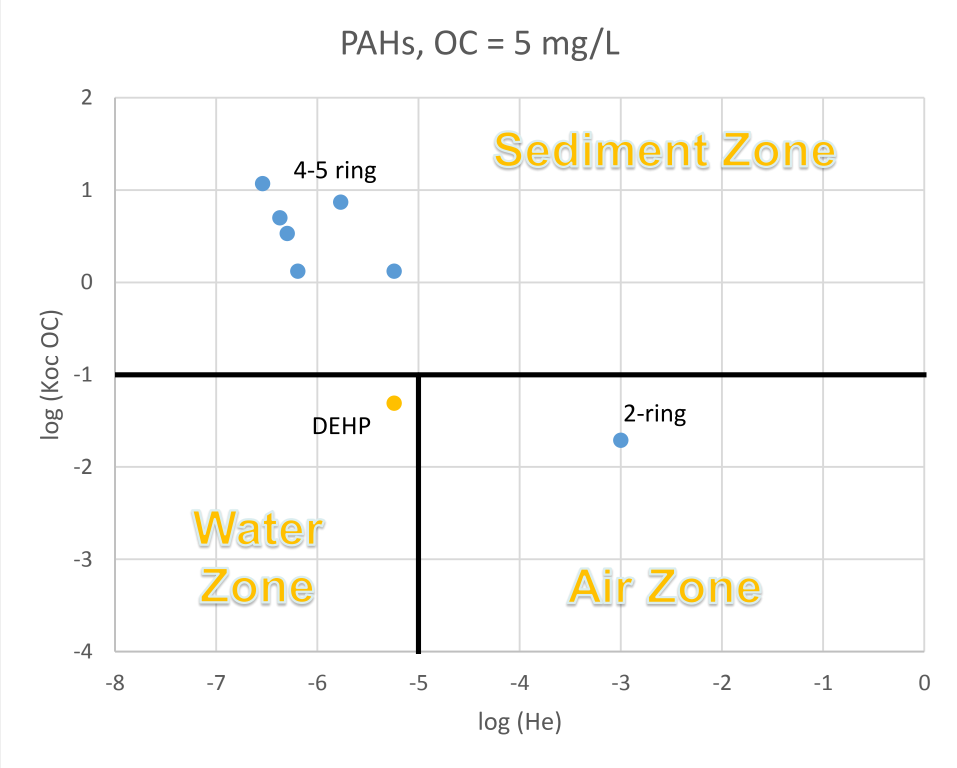
Chapra Model: PCBs and Dioxins



Mono- and Dichloro PCBs tend to volatilize; heavier congeners associated with sediment;
TCDD behaves very much like higher weight PCBs

Chapra Models: cPAHs and DEHP





Multi-ring cPAHs strongly sediment associated; water column primarily a source to sediment;
DEHP tends to remain in the water column

Implications for PCBs

- Large range of Koc and He constants; may be site-specific but little data available for LDW
  - Literature values have order-of-magnitude variability
  - Without site-specific data, need more generalized approach
- Can't model all 209 congeners; need reasonable grouping.
  - PCB homolog groups (number of chlorines) may provide a reasonable basis?
- Distinction in behavior between tri- and higher PCB homologs, versus mono- and dichloro homologs
- Dioxin-like PCBs mostly in higher weight class

Aroclors vs. PCB Congeners

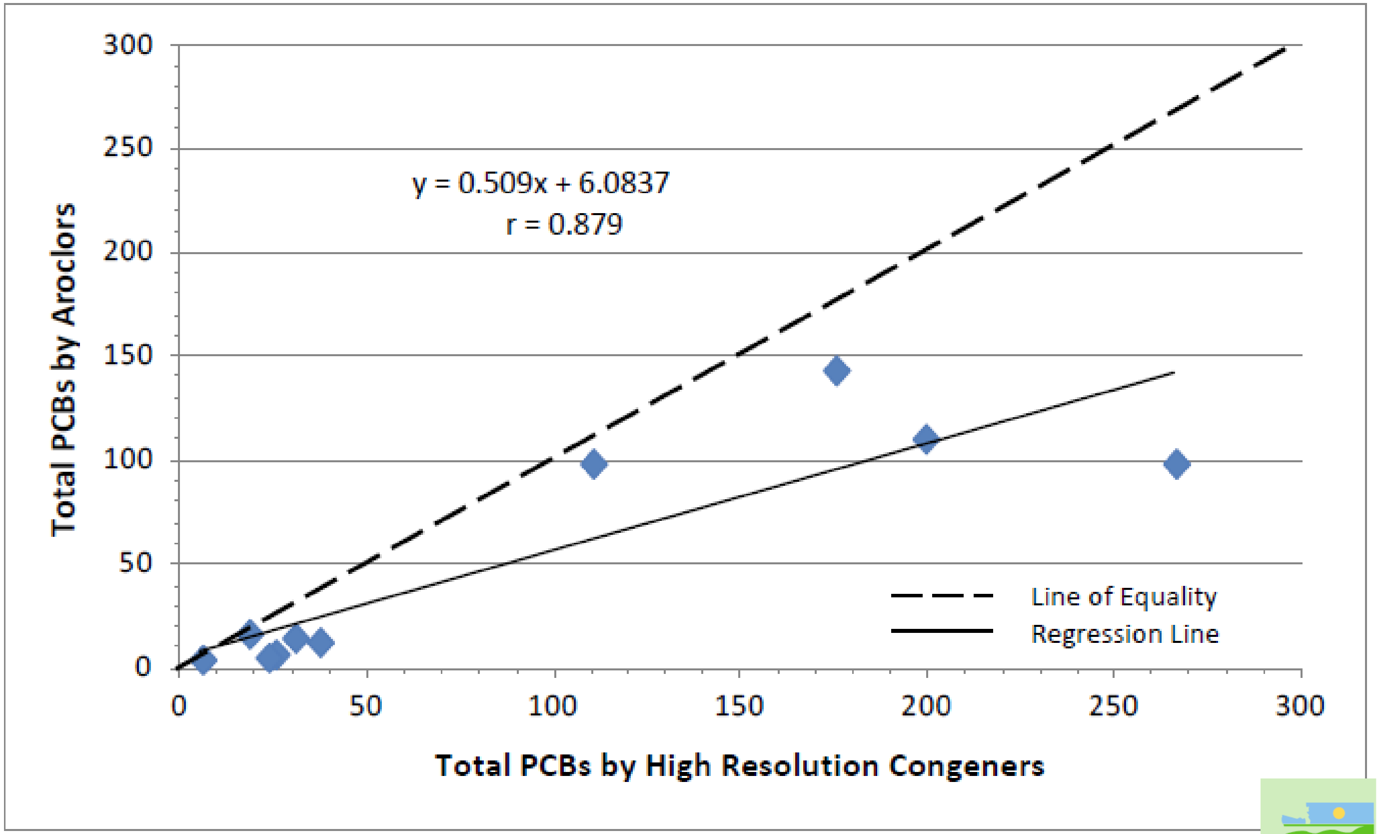


Figure 4. Total PCBs by High Resolution Congeners and Aroclor Analyses.

DEPARTMENT OF ECOLOGY
State of Washington

Publication No. 14-03-009

PCB Method Comparison of High and Low Resolution Sediment Analysis

Implications for Other Organics

- TCDD can be modeled like a high-weight PCB
  - Non-polar, similar partitioning, solubility
- cPAHs are expected mostly in sediment; water is mostly a source to the sediment
  - Low solubility, low volatility
- DEHP will have significant component in water
  - Higher solubility -> significant water phase
- Mercury requires a different approach from organics
  - MeHg not strongly lipophilic; methylation is key
- Arsenic, copper, and zinc:
  - Can focus on inorganic forms
  - Do we need to model free dissolved fraction (for toxicity)?
  - Do we need to model toxicity directly, accounting for biotic ligands?

Pollutant Behavior: Mercury, Arsenic, Copper, Zinc

- Ionic metals and a metalloid (arsenic)
  - Redox chemistry
  - Formation of insoluble compounds
  - Often controlled by sulfide, iron chemistry
- Toxicity:
  - Dissolved form key for arsenic, copper, zinc
  - Mercury bioaccumulation driven by organic methylmercury
    - Organic, but not strongly lipophilic
    - Formed by bacterial reduction in hypoxic sediments
    - Methylmercury data not available. Data support for food web modeling is questionable.

Key Data Gaps for Organic Pollutants

- Lacking paired data for site-specific determination of partition coefficients for PCBs, PAHs, TCDD
- Water column data for PCBs as Aroclors is problematic for comparison to congeners and homologs.
- Limited data to constrain release from and decay rates in sediment

Key Gaps for Metals/Metalloids

- Mercury: Lack MeHg data and information on factors that influence methylation (redox, sulfate balance)
- Ionic metals: Information on competing common ions incomplete to support redox chemistry

Questions and Discussion