

United States Department of the Interior

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April 15, 2016

Ron Timm Lower Duwamish Waterway Site Manager Toxics Cleanup Program Washington State Department of Ecology Northwest Regional Office

Hello Ron,

The purpose of this progress report is to document the place of progress before the project entitled "Assessing Sediment and Toxic Chemical Loads from the Green River, WA to the Lower Duwamish Waterway" was suspended in autumn 2015 owing to loss of funding for the State of Washington's Model Toxics Control Act (MTCA) program.

Between 2013 and 2015, the USGS collected samples of water, suspended sediment, and bed sediment from the Duwamish River at river mile 10.8 at USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA. The samples were analyzed for a large suite of toxic chemicals, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals including arsenic, and dioxins/furans. In addition, two new streamgages were installed – one at USGS 12113390 and one at river mile 6.3 at USGS 12113415 – Duwamish River at E. Marginal Way Br at Duwamish, WA. Both stations were reporting 15-minute, real-time data for stage, velocity, water temperature, turbidity, and specific conductance (specific conductance at the Marginal Way bridge only). Real-time discharge also was being reported at the Tukwila station, based on a rating curve developed during this project. The data – chemical concentrations in water, bound to suspended sediment, and in bed sediment and instantaneous loads - from these sampling efforts is published in two USGS Data Series (DS) reports:

DS 880 (<u>http://pubs.usgs.gov/ds/0880</u>) DS 973 (<u>https://pubs.er.usgs.gov/publication/ds973</u>).

In this progress report, we provide estimates of suspended-sediment loads and suspended sediment-bound chemical loads based on data collected from USGS 12113390. Estimates of suspended-sediment loads are determined from the regression between discrete samples of suspended-sediment concentration (SSC) or the fine suspended-sediment concentration (SSC_{FINES}) and continuous measurements of turbidity, per USGS methods (Rasmussen and others, 2009). Suspended sediment-bound chemical load estimates are calculated as the product of the above sediment loads and three summary statistics of sediment-bound chemical concentrations. The selected summary statistics are the 10th percentile, the median, and the 90th percentile of measured suspended sediment-bound chemical concentrations. The selected summary statistics are the 10th percentile, the median, and the 90th percentile of measured suspended sediment-bound chemical concentrations. The actual chemical loads to the Lower Duwamish Waterway from upstream sources transported by the Green/Duwamish River are expected to fall within this reported range of chemical load estimates.

The methods and results are described below and in the attached Excel spreadsheet.

These estimates are based on 27 samples of suspended-sediment chemistry, collected between February 2013 and February 2015 over a range of river discharge and turbidity conditions. Chemical load estimates could be improved upon with the collection of an additional 10-15 suspended-sediment chemistry samples over another 1-2 years to capture inter-year variability and under-represented conditions (i.e. summer storms). Alternate statistical methods could be utilized to describe the variability in suspended sediment-bound chemical concentrations owing to the complex interactions between multiple environmental drivers, such as streamflow, precipitation, seasonality, land use, dam operations, etc. The additional data and utilization of more sophisticated load estimation techniques would reduce the uncertainty of chemical load estimates. We believe this information is critical to the success of the Lower Duwamish Waterway sediment remediation activities that are currently underway. It also supports chemical- and sediment-source tracking efforts in the basin and provides input data for watershed pollutant loading models that are currently being developed for the Green/Duwamish basin.

Please feel free to contact us with any questions about this progress report. We have enjoyed collaborating with you to fill this important data gap, and hope to have the opportunity soon to report these load estimates in a formal publication and to continue the collaboration.

Sincerely,

Kathy Conn, Water-Quality Specialist Bob Black, Supervisory Hydrologist

Cc: Cindi Barton, Director, USGS Washington Water Science Center, Rick Dinicola, Associate Director, USGS Washington Water Science Center

Progress Report: Assessing Sediment and Toxic Chemical Loads from the Green River, WA to the Lower Duwamish Waterway

Prepared by the U.S. Geological Survey for the Washington State Department of Ecology

April 8, 2016

Background

Between 2013 and 2015, the USGS collected samples of water, suspended sediment, and bed sediment from the Duwamish River at river mile 10.8 at USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA. The samples were analyzed for a large suite of toxic chemicals, including polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), metals including arsenic, dioxins/furans, semivolatile compounds, pesticides, volatile compounds, butyl tins, hexavalent chromium, and organic carbon. In addition, two new streamgages were installed – one at river mile 10.8 at USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, and one at river mile 6.3 at USGS 12113415 – Duwamish River at E. Marginal Way Br at Duwamish, WA. Both stations were reporting 15-minute, real-time data for stage, velocity, water temperature, turbidity, and specific conductance (specific conductance at the Marginal Way bridge only). Realtime discharge also was being reported at the Tukwila station, based on a rating curve developed during this project. The data – chemical concentrations and instantaneous loads - from these sampling efforts is published in two USGS Data Series (DS) reports:

DS 880 (<u>http://pubs.usgs.gov/ds/0880</u>) DS 973 (<u>https://pubs.er.usgs.gov/publication/ds973</u>).

Purpose

The purpose of this progress report is to document the place of progress before the project was suspended in autumn 2015 owing to loss of funding for the State of Washington's Model Toxics Control Act (MTCA) program. In this progress report, we provide estimates of suspended-sediment loads and suspended sediment-bound chemical loads.

Field Data Collection

Discrete water samples for suspended-sediment concentration and particle-size distribution.

Between February 2013 and February 2015, 27 discrete samples of water were collected from USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, for the analysis of suspended-sediment concentration (SSC, the mass of sediment per volume of water, reported in mg/L) and fine suspended-sediment concentration (SSC_{FINES}, the mass of suspended sediment with a particle diameter less than 62.5 µm per volume of water, reported in mg/L). Water samples were collected using the Equal-Discharge Increment (EDI) method (Edwards and Glysson, 1999) with a D-96 sampler (Davis 2001) for an isokinetic depth- and flow-integrated composite sample. Samples were analyzed for SSC and particle size distribution (including the percent of fine sediment) at the USGS Cascades Volcano Observatory (CVO) in Vancouver, Washington, per USGS methods (Guy, 1969). Samples for SSC were collected over a range of conditions, with discharge ranging from 800 to 7200 cubic feet per second (cfs). SSC concentrations ranged from 6 mg/L to 555 mg/L (Sheet 1 in the corresponding Excel file). The percent fine sediment ranged from 56% to 95%, resulting in SSC_{FINES} concentrations ranging from 5 mg/L to 383 mg/L (Sheet 1). Instantaneous turbidity was measured mid-depth in the river thalweg during discrete SSC sampling using a hand-held multiparameter sonde (YSI 6820-V2, SonTek). The sonde was

calibrated in formazin-based standard before each sampling event, according to Wagner and others (2006).

Sheet 1. Suspended-sediment concentration, discharge, and turbidity during 27 sampling events, Duwamish River at Golf Course at Tukwila, WA, 2013-15.

Chemical analysis of discrete suspended-sediment samples

Between February 2013 and February 2015, 27 samples of suspended sediment were collected at USGS 12113390 by continuous-flow centrifugation for chemical analysis, using field protocols and laboratory analytical methodology as described in Conn and Black (2014) and Conn and others (2015). The samples were analyzed for a suite of chemical parameters, in the following priority order:

- Total organic carbon
- 209 PCB congeners
- Dioxins/furans
- Metals, including mercury
- Low-level PAHs
- Semivolatile compounds
- Butyl tins
- Hexavalent chromium
- Pesticides
- PCB Aroclors
- Volatile organic compounds

Summary statistics, determined in SYSTAT 13 (Systat Software, Inc.), of suspended-sediment chemistry results are compiled in Sheet 2 for compounds that were detected in 20% or more of samples. Three approaches for calculating summary statistics were used: traditional methods when there were no non-detects (i.e. 100 % detection), nonparametric Kaplan-Meier (K-M) methods when there were <50 % non-detects, and regression on order statistics (ROS) when there were 50-80 % non-detects, per Helsel (2005). Statistically-valid summary statistics could not calculated for chemicals that were not detected in more than 80% of samples (Sheet 3), which included all of the volatile organic compounds, pesticides, butyl tins, hexavalent chromium, and some of the semivolatile compounds, PCB congeners, dioxins/furans, and one metal (antimony).

Varying values were reported for non-detected chemicals (Conn and Black 2014, Conn and others 2015). Non-detects were reported at the reporting level (with a U qualifier) for all compounds except those determined by high-resolution mass spectrometry - the 209 PCB congeners and the dioxins/furans - for which non-detects were reported at the detection level (with a UJ qualifier). Estimated results between the detection level and the reporting level (with a J qualifier) were considered detections and included in the statistical calculations. Results that did not meet all of the high-resolution mass spectrometry quantification criteria (with an NJ qualifier) were not considered detections and were not included in the statistical calculations.

Sheet 2. Discrete suspended sediment-bound chemical concentrations and summary statistics, Duwamish River at Golf Course at Tukwila, WA, 2013-15.

Sheet 3. Chemicals detected in less than 20 percent of suspended-sediment samples, and for which no statistics or loads were calculated.

Time-series data (turbidity, discharge, stage, velocity, water temperature)

Continuous turbidity was measured at USGS 12113390 from November 2013 through June 2015, with the exception of intermittent periods when instrument failure occurred. Turbidity was measured using a DTS-12 nephelometric turbidity sensor (Forest Technology Systems, LTD) enclosed within a bank-mounted protective pipe that extended into the river channel. This mounting arrangement allowed turbidity measurements in an actively flowing part of the river channel and decreased the likelihood of debris accumulation around the sensor face or on the mounting hardware. The sensor was operated and maintained according to USGS protocols for continuous water-quality instruments (Wagner and others, 2006). The time-series turbidity record was processed, reviewed, and approved for the entire period of record per USGS protocols for continuous water-quality data (Wagner and others, 2006). Turbidity is reported as median 15-minute values from November 2013 through June 2015 (Sheet 4). Turbidity in the Duwamish River during the period of record rarely exceeded 250 Formazin Nephelometric Units (FNU) and was less than 10 FNU more than 75% of the time.

Sheet 4. Time-series data, including median 15-minute turbidity, discharge, stage, velocity, water temperature, and computed suspended-sediment concentration and load, Duwamish River at Golf Course at Tukwila, WA, November 2013 through June 2015.

Continuous discharge, in cfs, at USGS 12113390 was determined using the index velocity method (Levesque and Oberg, 2012). Data from the co-located acoustic Doppler velocity meter (ADVM) was indexed to derive a mean velocity for the cross-section. The indexed velocity was then used in conjunction with the stage-derived area to compute 15-minute forward or reverse discharge information past the tidally-influenced station. The period of record in this report (November 2013 through June 2015) includes approved discharge data from November 2013 through November 2014 and provisional discharge data since November 2014. Median 15-minute discharge at river mile 10.8 in the Duwamish River during the period of record ranged from -1110 cfs (the negative sign indicates reverse, or upstream, flow) to +9190 cfs (Sheet 4).

Additional co-collected time-series data (Sheet 4) include stage and velocity (approved through November 2014) and water temperature (approved through the period of record).

Filling in Gaps in Time-Series Records

A continuous time-series record of turbidity and (or) discharge is needed to calculate continuous SSC and suspended-sediment loads. The preferred method to calculate a continuous record of SSC is to use a turbidity-SSC regression. When turbidity time-series data is missing, continuous SSC can be calculated based on a discharge-SSC regression instead. Missing data, or gaps, in the turbidity and discharge time-series records occurred (Sheet 4). Some missing data occurred in short (≤ 6 hour) gaps owing to erratic turbidity sensor readings (spikes) or sensor maintenance. For these gaps less than or equal to six hours, when conditions were generally stable, a linear interpolation between the values before and after the gap was used to fill in the missing turbidity and discharge data (Sheet 4). Stable conditions were indicated by similar turbidity values before and after the gap and indicated by similar values of other time-series data during the gap.

There was one long period of rejected turbidity data from September 29 to December 3, 2014 owing to a slow optical failure of the turbidity sensor. The discharge record was used to calculate SSC during this period. Unfortunately, discharge was also missing during part of this period, from November 26 to December 5, 2014 because the ADVM was knocked askew by large debris during a high-flow event. A two-step process was used to fill the discharge gap between November 26 and December 3, 2014:

1. For stages greater than or equal to 12.5 ft., discharge was estimated from a discharge-stage linear regression. The 12.5-ft stage threshold was selected to reduce or eliminate the tidal influence on the stage readings. The regression was based on 1,574 observations of paired 15-minute discharge and stage values during the approved period of record (November 2013 to November 2014). The resulting regression had an R^2 of 0.961 (Figure 1).



Figure 1. Discharge-Stage regression, USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA.

2. When stage dropped below 12.5 ft., discharge was estimated from a linear regression with discharge from the next upstream discharge gage – USGS 12113000, Green River near Auburn, WA. The regression was based on 34,772 observations of paired 15-minute discharge values over all stages from both gages during the approved period of record (November 2013 to November 2014). The resulting regression had an R^2 of 0.944 (Figure 2).



Figure 2. Regression between discharge at USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA and discharge at USGS 12113000 – Green River near Auburn, WA.

From these procedures a continuous record of discharge was constructed (Figure 3).



Figure 3. Continuous record of discharge constructed from the original record (blue), estimated from stage (red), and estimated from discharge at the next upstream gage (green), Duwamish River at Golf Course at Tukwila, WA, November-December, 2014.

Regression Development

Four single linear regression models were developed using turbidity or discharge as the explanatory (x) variable and SSC or SSC_{FINES} as the response (y) variable.

SSC-Turbidity Regression

A regression equation was developed from the relation between discrete samples of SSC and continuous measurements of turbidity, per USGS methods (Rasmussen and others, 2009). The calibration data set was based on 23 pairs of SSC and turbidity sampled over a range of conditions (Figure 4).



Figure 4. Turbidity duration curve, USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, November 2013 – June 2015.

A median value of the 15-minute median turbidity values during the discrete SSC sampling window (typically 30-60 minutes) was used. When 15-minute median turbidity data was unavailable or suspect, values were estimated from a regression with instantaneous turbidity measured with a hand-held YSI with an R^2 of 0.998 (Figure 5).



Figure 5. Turbidity regression between instantaneous measurements with a YSI sonde (YSI) and 15-minute median values with a DTS-12 sensor (DTS-12), USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA.

A transformed least-squares regression model for the relation between discrete samples of SSC and continuous measurements of turbidity was selected based on analysis of diagnostic statistics and model residuals consistent with Rasmussen and others (2009). Both the SSC-turbidity model and the log(SSC)-log(turbidity) model showed linearity, high R² values (>0.9) and low standard errors. However, the variance of the residuals for the untransformed regression indicated a heteroscedastic pattern in which the variability of the residuals increased as estimated SSC values increased. The variance of the residuals for the log₁₀-transformed regression indicated a homoscedastic pattern and a more normal distribution. This resulted in a higher Probability Plot Correlation Coefficient (0.976 vs. 0.877) indicative of a relationship that meets the assumptions of a statistically valid regression model. The regression between log₁₀ SSC and log₁₀ turbidity had an R² of 0.947 (Figure 6).



Figure 6. Regression, with 90 percent confidence intervals, between log_{10} turbidity and log_{10} suspended-sediment concentration (SSC), USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, 2013-2015.

SSC_{FINES}-Turbidity Regression

A regression equation was developed from the relation between discrete measurements of SSC_{FINES} and continuous measurements of turbidity, similar to the SSC-turbidity regression described above. The calibration data set was based on 22 pairs of SSC_{FINES} and turbidity data. Similar to the SSC-turbidity regression, both the untransformed and the log₁₀ transformed

regressions performed well, but the log_{10} transformed regression was selected based on the more normal distribution of the variance of the residuals, as indicated by a higher Probability Plot Correlation Coefficient (0.978 vs. 0.949). The regression between log_{10} SSC_{FINES} and log_{10} turbidity had an R² or 0.910 (Figure 7).



Figure 7. Regression, with 90 percent confidence intervals, between log_{10} turbidity and log_{10} fine suspended-sediment concentration (SSC_{FINES}), USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, 2013-2015.

SSC-Discharge Regression

A regression equation was developed from the relation between discrete measurements of SSC and continuous measurements of discharge, similar to the SSC-turbidity regression described above. The calibration data set was based on 26 pairs of SSC and discharge collected over a range of conditions (Figure 8).



Figure 8. Discharge duration curve, USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, November 2013 – June 2015.

A median value of the 15-minute discharge values during the discrete SSC sampling window (typically 30-60 minutes) was used. When 15-minute discharge data was unavailable, instantaneous measurements of discharge were used instead. The regression between \log_{10} SSC and \log_{10} discharge was selected (Figure 9) based on the more normal distribution of the variance

of the residuals, as indicated by a higher Probability Plot Correlation Coefficient (0.986 vs. 0.962). The R² for this model was 0.666.



Figure 9. Regression, with 90 percent confidence intervals, between log₁₀ discharge (streamflow) and log₁₀ suspended-sediment concentration (SSC), USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, 2013-2015.

SSC_{FINES}-Discharge Regression

A regression equation was developed from the relation between discrete measurements of SSC_{FINES} and continuous measurements of discharge, similar to the SSC-turbidity regression described above. The calibration data set was based on 25 pairs of SSC_{FINES} and turbidity. The log_{10} transformed regression was selected and had an R² of 0.599 (Figure 10).



Figure 10. Regression, with 90 percent confidence intervals, between log₁₀ discharge (streamflow) and log₁₀ fine suspended-sediment concentration (SSC_{FINES}), USGS 12113390 – Duwamish River at Golf Course at Tukwila, WA, 2013-2015.

Time-Series Suspended-Sediment Concentration and Load Calculations

A continuous record of SSC (at 15-minute time steps) from November 2013 through June 2015 was determined from the retransformed \log_{10} SSC – \log_{10} turbidity regression and corrected for bias resulting from the log transformation.

During the turbidity gap from September 29, 2014 through December 3, 2014, the retransformed log_{10} SSC – log_{10} Discharge regression was also corrected for transformation bias.

The resulting SSC time-series is reported in Sheet 4. During the 581-day period of record, the calculated SSC ranged from a minimum of -11.4 mg/L (the negative sign indicates upstream sediment transport) to a maximum of 2,263 mg/L, with a median of 10.8 mg/L (Sheet 4). The SSC values were converted to 15-minute suspended-sediment loads (SSL). The total SSL during the 581-d period of record was 174,210 tons (U.S. tons), resulting in an average of 300 tons/d and 109,443 tons/year (Sheet 4). This is within the range, though on the low end, of previously-reported estimates of sediment load, which have ranged from approximately 50,000 tons/year to 500,000 tons/year (Embrey and Frans 2003, LDWG 2008). This period of record was one of the driest on record, and captured only one complete wet season. Also, the total SSL value incorporated the upstream sediment load (total = downstream - upstream). Finally, the SSL also only reports the suspended-sediment load, and does not include an estimate of bedload transport, which is highly variable and may contribute essentially no additional load during low-flow conditions and a large additional sediment load under high-flow conditions.

The process was repeated to determine a continuous record of SSC_{FINES} (at 15-minute time steps) for the same period of record. The resulting SSC_{FINES} time-series is reported in Sheet 4. During the 581-d period of record, the calculated SSC_{FINES} ranged from a minimum of -10.1 mg/L (the negative sign indicates upstream sediment transport) to a maximum of 1399 mg/L, with a median of 8.8 mg/L (Sheet 4). The SSC_{FINES} values were converted to 15-minute fine suspended-sediment loads (SSL_{FINES}). The total SSL_{FINES} during the 581-d period of record was 123,615 tons (U.S. tons), resulting in an average of 213 tons/d and 77,658 tons/year (Sheet 4). On average, approximately 71 % of the total suspended-sediment load was comprised of fine particles less than 62.5 μ m in diameter.

Suspended Sediment-Bound Chemical Concentration Ranges and Load Calculations

Suspended sediment-bound chemical load estimates were calculated as the product of the above sediment loads and three suspended sediment chemistry summary statistics – the 10th percentile, the median, and the 90th percentile - of sediment-bound chemical concentrations (see Sheet 2). A potential range of annual suspended sediment-bound loads for each chemical is summarized in Sheet 5. Four values are reported for each chemical:

- a low-end bound, based on the product of the 10th percentile chemical concentration and the SSC_{FINES} load, which assumes the chemical is only bound to fine particles,
- a median (SSC $_{\rm FINES}$) value, based on the product of the median chemical concentration and the SSC $_{\rm FINES}$ load,
- a median (SSC) value, based on the product of the median chemical concentration and the SSC load,

- a high-end bound, based on the product of the 90th percentile chemical concentration and the SSC load, which assumes the chemical is bound to all particle sizes.

Sheet 5. Range of annual suspended sediment-bound chemical loads, based on data collected from 2013 to 2015, Duwamish River at Golf Course at Tukwila, WA.

Chemical loads were calculated using both the SSC and SSC_{FINES} loads because many chemicals prefer to sorb to fine sediment, and sorption decreases with increasing particle size. Actual chemical loads to the Lower Duwamish Waterway from upstream sources transported by the Green/Duwamish River are expected to fall between the low-end and the high-end values.

A potential range of annual suspended sediment-bound chemical loads for the four contaminants of concern in the Lower Duwamish Waterway are:

Statistic used to calculate annual chemical load	Arsenic	cPAHs	Dioxins / Furans	PCBs
	(kg)	(g TEQ)	(mg TEQ)	(g)
10% (SSC _{FINES})	587	761	59.9	61.2
Median (SSC FINES)	874	3,411	218	335
Median (SSC)	1,231	4,807	307	473
90% (SSC)	2,464	17,892	1,213	2,691

Chemical load estimates could be improved upon with the collection of an additional 10-15 suspended-sediment chemistry samples over another 1-2 years to capture inter-year variability and under-represented conditions in the current data set (for example, summer storms). Alternate statistical methods could be utilized to describe the variability in suspended sediment-bound chemical concentrations owing to the complex interactions between multiple environmental drivers, such as streamflow, precipitation, seasonality, land use, dam operations, etc. The additional data and utilization of more sophisticated load estimation techniques would reduce the uncertainty of chemical load estimates. This information is likely to be critical to the success of the Lower Duwamish Waterway sediment remediation activities that are currently underway. It also supports chemical- and sediment-source tracking efforts in the basin and provides input data for watershed pollutant loading models that are currently being developed for the Green/Duwamish basin.

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