Memorandum

To: Elissa Ostergaard, Miller-Walker Creeks Basin Steward

CC: Jim Simmonds, King County Water Quality and Quantity Supervisor

From: Jenée Colton, King County Water Quality Planner

Date: 3/15/2013

Re: 2012 Miller/Walker Creek Coho Prespawn Mortality Study

King County conducted a water chemistry and toxicity study in 2012 to further investigate the potential cause(s) of coho prespawn mortality. The study collected two baseflow samples and eight grab samples in a time series during each of two storm events (October 15 and October 22). Samples were collected at the 13th Ave Bridge crossing in Miller Creek. All samples were analyzed for conventional parameters, minerals and the following metals in dissolved form: arsenic, cadmium, chromium, copper, lead, nickel, silver, and zinc. The storm samples were all tested for toxicity using bioassays of two animal species, *Daphnia pulex* (a water flea) and *Pimephales promelas* (fathead minnow). A toxicity identification evaluation (TIE) test was planned for any samples observed to cause mortality with the intent to determine if metals are causing the observed toxicity. Details of the study methods are located in the project Sampling and Analysis Plan (King County 2012).

Water Chemistry Results

All of the chemistry results can be found in the King County Environmental Laboratory (KCEL) Laboratory Information Management System (LIMS) database under the locator "MILLER_13THAVE", using the year 2012 to limit the date field. Generally, conventionals look normal. I checked temperature, pH and DO against the acute water quality standards. Dissolved oxygen and pH are normal and do not exceed the state standards. Water temperature exceeded the standard, which is a 7-day average daily maximum, during the first storm. I suspect Miller Creek gets warm in the summer and exceeds the standard for spawning salmon and trout during the daytime. The first rains likely cool down the water and I think we saw that occurring in the first storm we sampled. By the second storm we sampled, the water temperature had cooled below the standard.

To follow up on the dissolved organic carbon (DOC) quality theory, after the 2011 DOC study, I talked with one of the modelers who developed the current BLM (biotic ligand model) software and knows metals toxicity intimately, Robert Santore. I shared the story of PSM with him and discussed the potential that DOC quality may be a factor. He explained that he had worked on addressing this question of DOC quality influencing metals toxicity with the scientists who research DOC quality and they came to the conclusion that DOC quality was only important under extreme conditions of pH and hardness, which we don't have here in PSM streams. Santore convinced me that DOC quality could not explain

PSM so I stopped pursuing that angle. We did not measure DOC quality in the 2012 study but the 2011 results showed that DOC quality in Miller Creek was only slightly lower (and relatively good) during storms than baseflow. This was inconsistent with the large differences observed in DOC quality in storms compared to baseflow at Longfellow Creek and a reference stream in 2010 and does not support the DOC quality theory.

Of the metals, cadmium and silver were not detected in any samples. All other metals were detected in all samples. Metal concentrations were higher during storm events than at baseflow. Metal concentrations measured during the two storm events generally showed an increasing trend over the time period of sampling. For example, Figures 1 and 2 show change in Miller Creek copper and zinc concentrations during baseflow and over approximately four hours of the October 15, 2012 storm. Although metals concentrations increased over the sampled storm events, concentrations did not exceed the Acute Washington State Water Quality Standards (WQS) for protection of aquatic life in freshwater. Note that the WQS for metals are hardness dependent and, therefore, change over time and under different water conditions. The acute WQS for copper was nearly exceeded by the end of the October 15th storm sampling (Figure 3). The lack of WQS exceedance is consistent with water chemistry results for other creeks (King County unpublished, McCarthy et al. 2008, Sholz et al. 2011). The WQS are thresholds that can be used to predict toxicity but in the case of prespawn mortality, WQS and other published toxicity thresholds have not proven useful; the toxicity thresholds are not being exceeded, yet coho are clearly experiencing acute toxicity. Toxicity studies have tested coho species at various life stages but not a life stage that represents coho undergoing prespawn mortality, i.e., as spawning adults under the stress of migration, physiological shifts due to moving from saltwater to freshwater, poor urban stream habitat, and the poor water quality of stormwater runoff. In addition to the natural stress of migrating to freshwater streams from the ocean, returning coho must navigate

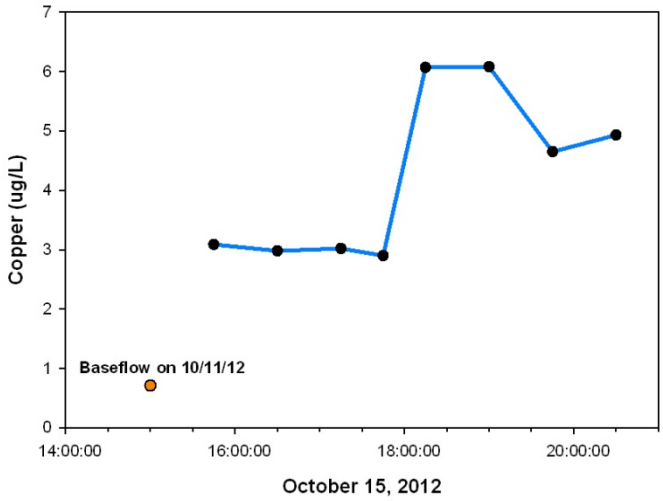

Figure 1. Miller Creek Copper Concentrations Baseflow and During the October 15th Storm.

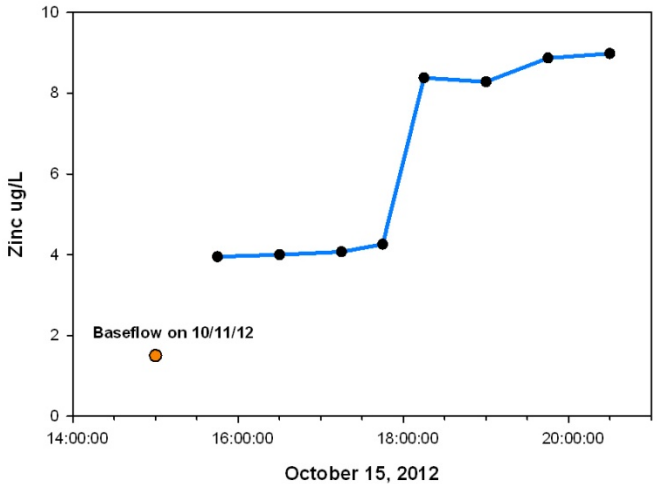

Figure 2. Miller Creek Zinc Concentrations Baseflow and During the October 15th Storm.

the urban waterways that not only carry stormwater runoff, but are also modified habitats themselves with channelized stream beds, few if any resting places, and small estuaries for physiological transition. The combination of natural and urban stressors experienced by returning salmon may result in their being extremely sensitive compared to other species and coho at earlier life stages. Therefore, it can't be assumed that existing toxicity thresholds are protective of coho in prespawn mortality streams. Until more information is available, little weight should be placed on a lack of exceedance of WQS or other toxicity thresholds.

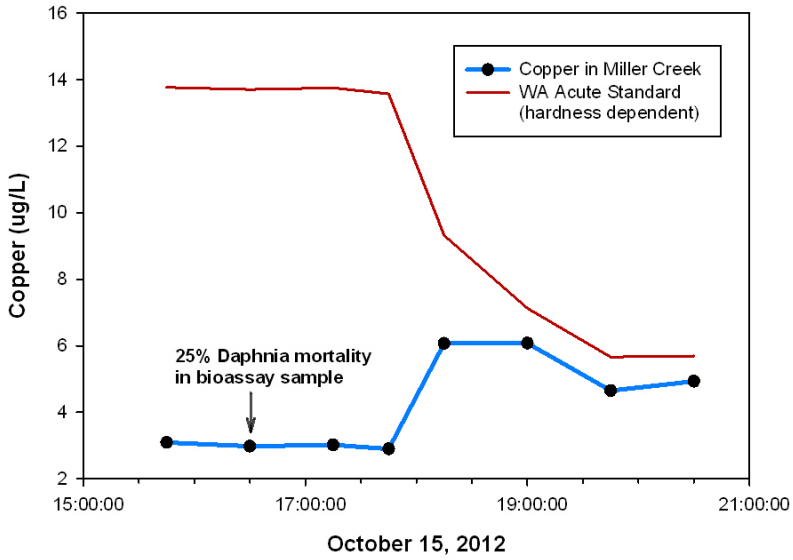

Figure 3. Storm Copper Concentrations in Miller Creek Compared to the WA Acute WQS (Daphnid toxicity occurred where noted)

Nutrient ions (i.e., minerals) such as calcium, chloride, and sodium (Ca^{2+}, Cl^{-}, Na^{+}) play an important role in metals toxicity. Metals use the same pathways as these ions to enter cells in the gill in a kind of mimicry. Metals compete with the nutrient ions for these pathways which can result in reduced uptake and an imbalance of nutrient ions, loss of electrolytes and circulatory collapse (Wood, 2012). Thus, higher concentrations of nutrient ions in the water will improve the ability of the fish's gill cells to compete against the dissolved metals in the water and avoid metals toxicity. The chemistry of water from prespawn mortality streams during storms has consistently shown a decrease in calcium, hardness (directly related to calcium carbonate), sodium, and magnesium and other ions. The loss of nutrient ions in the water concurrent with increases in metals concentrations creates a higher risk of metals toxicity. The ion concentrations measured in Miller Creek during storms also showed a decrease in concentration over the sampling period (Figure 4).

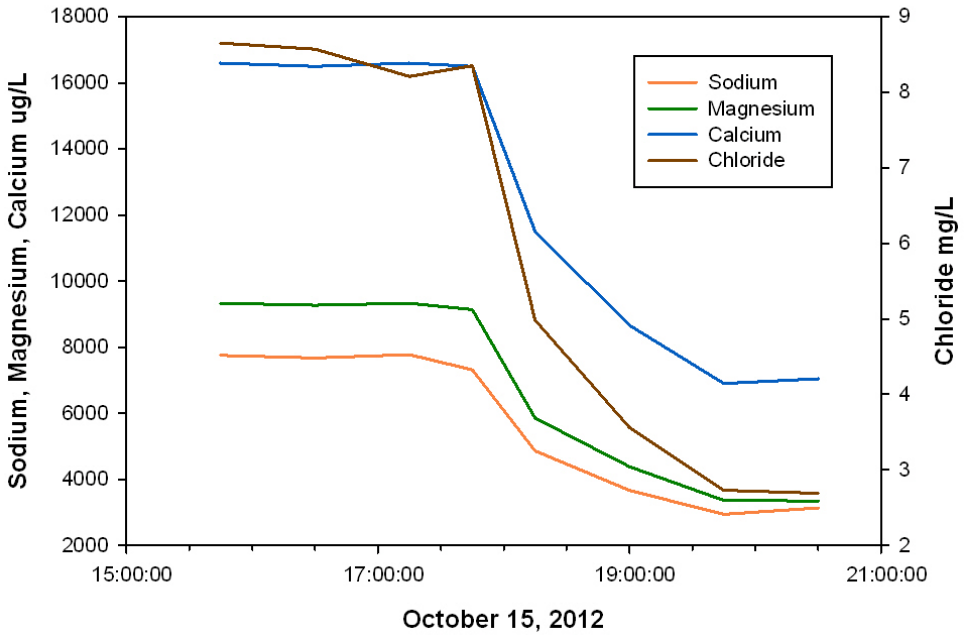

Figure 4. Nutrient Ion Concentrations in Miller Creek During the October 15th Storm

Continuous flow data were downloaded for the Miller Creek gage located at the Miller Creek Sewer Plant in Normandy Park (42aa) to document corresponding flow during the storms sampled. The first storm sampled occurred following a larger event and sampling successfully captured the peak flow (Figure 5). It is possible that metals concentrations may have been higher if the larger, earlier storm were sampled.

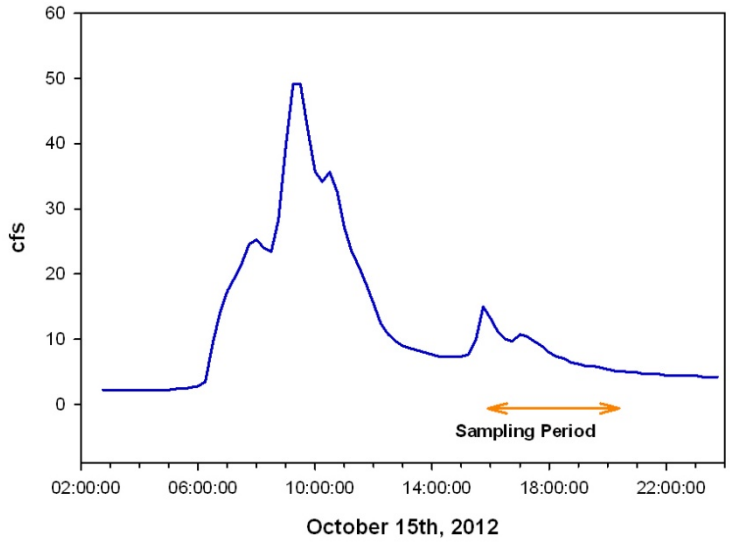

Figure 5. Flow at Miller Creek Gage 44A for October 15, 2012 Storm

Toxicity Testing Results

Mortality of fathead minnows was not observed in any samples during bioassay testing. In one sample from the first storm event, 25% mortality was observed in the water flea. This sample was the second collected in a series of eight samples. Interestingly, the timing of this sample does not correspond with an increase in metals concentrations (Figure 3). The increase in copper concentration occurred later during the storm event; this timing was consistent for other metals as well.

The sample with the associated 25% water flea mortality was tested using the TIE. The metal-removing agent, EDTA, did not reduce toxicity to the water flea. The metal-removing agent, STS, reduced mortality in the sample to zero. EDTA is very effective at reducing the toxicity of copper, cadmium, mercury, lead, nickel, and zinc. However, because EDTA did not reduce toxicity to the water flea, these results indicate the toxicity was not caused by any of these six metals. Removal of toxicity by STS indicates toxicity was caused by either silver chloride or sodium selenate. This result is unexpected for multiple reasons. The first reason is that copper, cadmium, mercury, lead, nickel and zinc are contaminants frequently implicated in metals toxicity and are found at elevated concentrations in stormwater runoff; these were the most likely suspects. The second reason is that silver and selenium are unusual as toxic metals. Silver is very toxic to aquatic life but has very low water solubility making its environmental concentrations naturally relatively low. Selenium has a very low toxicity to aquatic life and the concentrations seen even at contaminated sites are orders of magnitude lower than the levels documented to be toxic. The third reason is that the common sources of silver (jewelry, coin, photography and mirror-making) and selenium (metal, phosphate and coal mining, coal plant wastes, petroleum refinery wastewater) are uncommon in the greater Seattle urban area. However, there are some known sources of silver associated with vehicles such as fuel sensors and diesel fuel. Silver was not detected in any baseflow or storm samples at the detection limit of 0.04 µg/L. Silver may be present at concentrations below this detection limit. Selenium was not analyzed in this study.

Discussion and Recommendations

Conventionals data appeared normal except for warm water temperatures exceeding WA WQS during the first storm; water temperature cooled to below the standard by the second storm event. Detected metals concentrations increased in storm events compared to baseflow in Miller Creek. Metals concentrations did not exceed WQS; however, it is believed the existing toxicity thresholds are not protective of coho undergoing prespawn mortality. Thus, comparison to WQS is of limited value. The nutrient ions calcium, sodium, magnesium, potassium and chloride decreased during storm events. This decrease in nutrient ions combined with the concurrent increase in metals concentrations creates a higher risk for metals toxicity in fish.

One sample in the first storm event caused 25% mortality to the water flea, *Daphnia pulex*. The TIE test results indicate that the toxicity may be caused by silver chloride or sodium selenate. Silver and selenium are unusual and unexpected suspects for metals toxicity. Silver is very toxic but does not dissolve easily in water. Selenium has very low toxicity. Typical sources of either silver or selenium are not found in substantial number in the Greater Seattle area. On the other hand, the cause of prespawn

mortality is unclear even with substantial information collected relating to the problem including pathology, physiology, chemistry and toxicology data. The specific causative agent(s) of prespawn mortality have not been identified yet. Thus, it is prudent to consider all possibilities thoroughly until information arises to definitively rule them out.

Two new key findings related to prespawn mortality and communicated to me via Jay Davis (USFWS) are that 1) exposure of adult healthy coho to 100% 520-Bridge runoff induced the symptoms of prespawn mortality and 2) blood samples taken from coho that died from prespawn mortality and control fish showed prespawn mortality coho blood is hemoconcentrated compared to control blood. Hemoconcentrated means there are more red blood cells per volume of blood than normal. This can also be described as having high hematocrit. High hematocrit indicates some kind of fluid imbalance such as dehydration. I was told that the concentrations of ions in the blood samples were highly variable but not consistently different between prespawn mortality and control samples which is counter to what is expected from an ionic imbalance caused by classic metals toxicity. However, the researchers who conducted this work have not finished analyzing their data and summarizing their conclusions. The main thinkers on this problem will be convening in March or April to discuss the most recent results. I plan to keep in touch with Jay Davis and I have shared with him King County's recent results of the toxicity testing discussed herein.

For the upcoming coho season, there are a couple possibilities for further work. We could follow up on these recent results and pursue the possibility that silver or selenium could be a cause of prespawn mortality. Silver seems more likely given its high toxicity and effect of causing high hematocrit. Being able to replicate the daphnid toxicity and removal by STS would demonstrate that our observations were not simply rare and unrelated to prespawn mortality. This would call for repeating the design used in 2012, without the fathead minnow bioassays. In other words, we would collect water samples in a time series during storm events for chemistry analysis and bioassay testing using *Daphnia pulex*. We could enhance the chances of sampling maximal contaminant concentrations by collecting water directly from, if possible, a stormwater discharge pipe entering Miller/Walker Creeks. I have talked to KCEL and determined that they can reduce the detection limit for silver to 0.005 ug/L from 0.04 ug/L. Also, they are able to add selenium to the analyte list at the same detection limit. I will talk to Jen McIntyre to see if she detected silver and at what level in the 520-Bridge runoff samples.

Another possibility is to try to set up a PSM coho isolation and treatment experiment where we find PSM symptomatic fish, isolate them and treat them with either calcium carbonate to test for metals toxicity in general, or with STS to test for silver/selenium, or both. This work would likely require a WDFW permit and probably an Ecology permit. It will also necessitate bringing in expertise from our fisheries staff and designing holding containers and a dosing treatment, etc. We will have to discuss the funding options for this work as I anticipate it will require more funding and difference sources than the budget spent last year, particularly for labor.

As the next few months progress, I hope to gain more information on the findings of NOAA and USFWS. I will keep options open for future work and we can discuss the best course of action.

References:

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