Zinc and Copper Concentrations in an Industrial Area Creek during Storm Events

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Zinc and Copper Concentrations in an Industrial Area Creek during Storm Events

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303(d) listing 2004 submittals:
Mill Creek at Orillia – dissolved oxygen and fecal coliform

Waterbody Number: WA-09-1015

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Abstract

Many industrial facilities statewide under the Industrial Stormwater General Permit (ISGP) have been found to discharge stormwater with elevated levels of zinc and copper. Mill Creek in Kent, Washington is in an industrialized urban area with a large number of facilities discharging stormwater under the ISGP.

Water quality monitoring of Mill Creek during three storm events showed exceedances of zinc and copper acute water quality criteria specified in the Washington State Water Quality Standards. The monitoring took place in the fall of 2005 for conditions approaching worst case, the "first flush" of runoff from a storm event following a period of no precipitation.

Exceedances of criteria were found for zinc during two storm events and for copper during one event. Concentrations of dissolved zinc and copper were found to be as high as 100 µg/L and 10.4 µg/L, respectively. Concentrations of total recoverable zinc and copper were as high as 105 µg/L and 14.1 µg/L.

There are indications that industrial stormwater discharges with elevated levels of zinc and copper may be the principal cause of water quality criteria exceedances in Mill Creek during storm events.

Acknowledgements

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- Douglas Henderson, King County METRO, for providing information and raw data for the 2001-2002 King County Green-Duwamish Watershed Water Quality Assessment.

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Introduction

Self-monitoring data, first required in 2003 under the Industrial Stormwater General Permit (ISGP), show elevated levels of zinc and copper in industrial stormwater discharges. Greater than 55% of industrial stormwater discharge samples have exceeded the zinc benchmark of 117 µg/L with 21% exceeding the action level of 372 µg/L. Self-reported data for copper shows somewhat lower rates of exceedances: 21% exceeding the benchmark of 63.9 µg/L and 6% exceeding the action level of 149 µg/L (Herrera, 2006).

Benchmark values which appear in the ISGP are stormwater discharge concentrations below which it is presumed that receiving water quality criteria will not be exceeded. When stormwater discharge concentrations are greater than the benchmark value, in the absence of receiving water information, the impact on receiving water quality is unknown. Exceeding action levels triggers a process whereby the permittee is to take action to reduce stormwater discharge metals concentrations.

Mill Creek in Kent, Washington was chosen for this 2005 case study of a receiving water because of the high density of industrial facilities in its drainage area. Exceedances of water quality criteria in Mill Creek would indicate the potential for exceedances in other urban receiving waters in industrial areas. Sampling was to take place during the worst-case condition of first flush of stormwater runoff from exposed surfaces after a period of no precipitation.

A secondary objective of this study was to develop extensive time-series data for several storm events under worst-case, first-flush conditions. The data, which include continuous receiving water flow, may prove useful for other studies.

Prior Assessments of Mill Creek Water Quality

The 1996 and 1998 Section 303(d) list of impaired waterbodies included the following parameters for Springbrook (Mill) Creek: fecal coliform, temperature, dissolved oxygen, sediment bioassay, cadmium, copper, mercury, and zinc. In addition, chromium was included in the 1998 list, having been incorrectly assigned to another segment in the 1996 list. Zinc was listed for two segments of Springbrook (Mill) Creek based on two excursions from water quality criteria in 1984.

The listings for cadmium, copper, mercury, zinc, and chromium were based on data from 1990 and earlier, before the superfund cleanup of Western Processing Co., Inc. Western Processing's activities had included recycling, reclaiming, treating, and disposing of industrial wastes, including electroplating wastes. Monitoring studies have confirmed the site is no longer a significant source of metals to Mill Creek.

Based on a review of more recent receiving water data from King County and Landau and Associates, Johnson and Golding (2002) concluded that Mill Creek is meeting criteria for metals including copper and zinc, and they recommended that the listings be removed from the 2002/2004 list. However, the data reviewed by Johnson and Golding were not collected during storm events. It was not until a 2003 King County study that receiving water data in the Mill Creek drainage area were obtained during storm conditions.

From 2001-2003, Herrera Environmental Consultants monitored receiving waters as part of a King County water quality study of the Green/Duwamish watershed (WRIA 9). The study was conducted to develop and prioritize management actions for a salmon habitat plan (King County, 2004).

In the study, a suite of metals was monitored in a sub-drainage area of Mill Creek at station B317 (shown in Figure 1). Sampling was limited to individual grabs taken one to three times per day during baseflow and storm events. Thirty-six samples were collected during 18 events. Of these, four showed excursions from freshwater acute water quality criteria for dissolved zinc during storm events. No samples showed excursions for copper (Table 1).

Table 1. King County (2004) study: Excursions from water quality standards, sampling site B-317.

Date	Flow (cfs)	Hardness (mg/L)	Zinc, Dissolved (µg/L)	Acute Water Quality Criterion (µg/L)
7 November 2002	6.9	38.3	52	50.8
21 January 2003	40	23.8	35.3	33.9
22 January 2003	75	24.1	34.6	34.3
17 November 2003	16	19.3	29.6	28.4

The drainage area contributing to streamflow at station B317 coincides roughly with that of the Mill Creek 76th Avenue outfall. An estimated 53% of the drainage area consists of industrial land use, greater than that of the overall Mill Creek drainage area (44% -Table 2).

Project Description

Water quality monitoring was conducted during three storm events in the fall of 2005. An automatic sequential sampler collected hourly samples of creek water. Sampling began just prior to each storm and was carried through peak streamflow. Total recoverable and dissolved forms of zinc and copper were monitored, as well as hardness and turbidity. Continuous streamflow data were also recorded.

Study Design

Site Selection

Mill Creek, near its confluence with Springbrook Creek in Kent, was selected as the monitoring site for the study because of the high density of industrial development in its drainage area (Figure 1). Fifty-six facilities with Department of Ecology permits under the ISGP are located within an 11.5 square mile portion of the Springbrook Creek/Mill Creek drainage area. Mill Creek proper has a drainage area of 7.9 square miles.

The Mill Creek drainage was the site of a 2005 survey of 28 industrial facilities (Golding, 2006). Self-reported industrial stormwater discharges from those facilities had a median zinc concentration of 196 µg/L, compared with the benchmark of 117 µg/L.

The three shaded areas of Figure 1 represent the sub-drainage areas that comprise the Mill Creek drainage area as defined on city of Kent Department of Public Works water resource maps.

Table 2 shows distributions of land use for the three sub-drainage areas as estimated from drainage area maps, aerial photographs, and city zoning map.

Table 2. Mill Creek sub-drainage areas and estimated percentages by land use.

Sub-Area	Lower Mill Creek ($4.0\ mi^2$)	76^{th} Ave Outfall ($1.1\ mi^2$)	Upper Mill Creek ($2.8\ mi^2$)	Overall Drainage Area ($7.9\ mi^2$)
Industrial	72%	53%	0%	44%
Downtown/ Commercial	11%	23%	0%	9%
Residential	0%	12%	67%	25%
Vegetated Areas	17%	12%	33%	22%

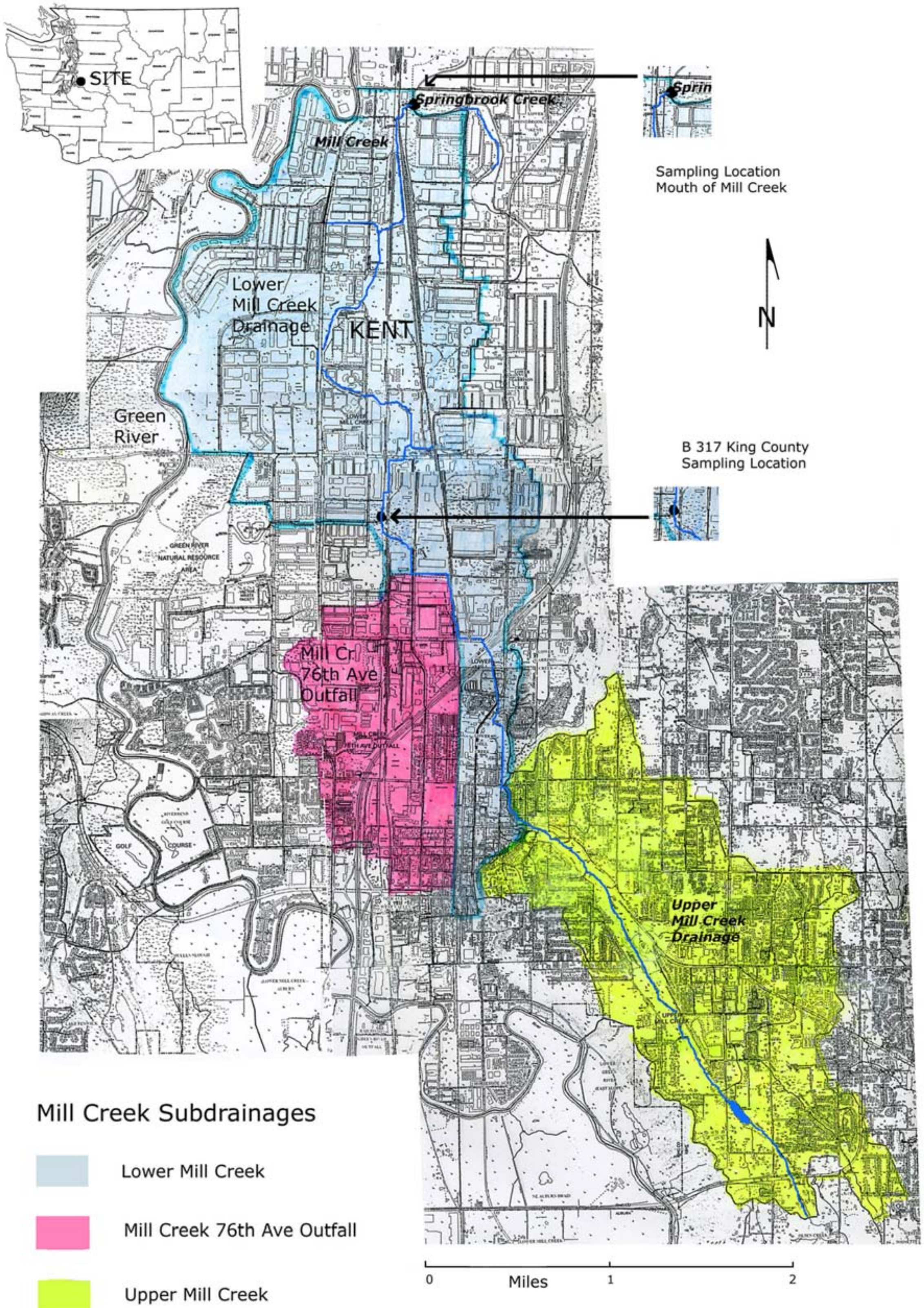

Figure 1. Mill Creek drainage area study site

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Monitoring Design

Stream monitoring was to take place during three storm events in the fall of 2005: August 28-29, September 29-October 1, and December 19-20. Each of these sampling periods followed a period of no significant precipitation. The initial stormwater runoff after a period of dry weather is considered to produce worst-case conditions in receiving waters during a storm event. An effort was made to monitor the first storm event following the long, dry summer season.

Measurements of streamflow for the monitoring site were available through a permanent U.S. Geographical Survey (USGS) gage station (12113349) located at the mouth of Mill Creek, coinciding with the sampling site location. The station provides real-time, continuous data at: http://waterdata.usgs.gov/wa/nwis/uv?station=12113349 . Historic flow data for the station are also available at the web site.

An increase in measured flow above background flow at the mouth of Mill Creek indicated the effective beginning of a storm event. Streamflow data throughout each storm were plotted with other study data to show their relationships throughout each storm event.

Monitoring was conducted to compare results with acute water quality criteria. Acute criteria are applied as a one-hour average concentration not to be exceeded more than once every three years on the average. The effects of stormwater runoff on receiving waters are typically of a short duration, and acute criteria are applied. Water quality criteria for metals apply to their dissolved form (Ecology, 2003).

Parameters monitored were:

- Zinc, total recoverable and dissolved
- Copper, total recoverable and dissolved
- Hardness
- Turbidity
- Streamflow

Zinc and copper were analyzed as recoverable (total) and dissolved. Total metals are reported by each facility under the ISGP self-monitoring requirements. Benchmarks and action levels specified in the ISGP are also as total metals.

The water quality criteria for zinc and copper are dependent on hardness. Turbidity, an indication of the cloudiness of a water sample, was determined with a field turbidimeter.

Sample Collection

Samples were collected with a Teledyne ISCO automatic portable sampler. The sampler was set to collect one composite sample per hour. Each composite sample was comprised of four sub-samples taken at 15-minute intervals. Each sample represented hourly metals concentrations in the receiving water.

The sampler was set up along the Interurban Trail on a pedestrian bridge over Mill Creek approximately 500 feet from the mouth of Mill Creek. The sampler intake hose was suspended upstream of the bridge from a 10-foot length of PVC, upstream of a drip line from a galvanized steel railing of the bridge (Figure 2). A pre-cleaned stainless steel strainer was attached at the intake opening of the sampler's Teflon® sampling hose. The strainer was suspended in a well-mixed portion of the creek, well above the creek bed to prevent the collection of sediments.

Figure 2. Setup of the portable sampler on the Interurban Trail pedestrian bridge.

During the days prior to a sampling event, real-time flow graphs for the USGS gage station were reviewed to verify periods of low, constant streamflow indicating a period of no precipitation. The decision to deploy the sampler was based on local weather forecasts. The sampler was started manually. Dates and times of sample collection are shown in Appendix A.

The day following the start of sampling, the base of the sampler unit was opened to access sample bottles. If a storm event began later than expected as shown by real-time streamflow, initial samples would be discarded. Samples chosen for analysis began with those collected several hours prior to a rise in streamflow.

The first storm event was sampled for 24 hours. During the later portion of the other storm events, some bottles were skipped to provide for a longer sampling period with the same number of analyzed samples. After each 24 hours of sampling, the sampler base was swapped out with a second base holding pre-cleaned bottles.

Prior to sampling, the 24 wedge-shaped polyethylene sample bottles were pre-cleaned with a solution of Liquinox® detergent, followed by 10% nitric acid rinse and three rinses with deionized water. The sampler was cleaned in the same manner by pumping the solutions through the Teflon®-lined sampler tubing. The flexible silastic tubing of the peristaltic pump was replaced with a new segment before each sampling event. The sampler base was filled with ice to cool samples during the collection period.

Samples for dissolved metals were filtered in the field through a pre-cleaned 0.45 µm Nalgene filter unit (#450-00045, type S). Each sample was transferred to a standard HDPE sample bottle. All metals samples were preserved to pH<2 with sub-boiled 1:1 nitric acid, carried in small Teflon® bottles. Teflon acid vials and Nalgene filters were cleaned at Manchester Laboratory as described by Kammin et al. (1995). Powder-free nitrile gloves were worn by personnel during filtering and when handling sample containers.

Each sample was given an ID number, tagged, and kept on ice, then cooled to 4ºC. Chain-of-custody procedures were observed and samples were delivered to the laboratory within allowable holding times for each parameter.

A summary of parameters, collection containers, sample preservation, and holding times appears in Table 3.

Table 3. Sample size, container, preservation, and holding time by parameter.

Parameter	Sample Size	Container	Preservation	Holding Time
Zinc, Copper (total recoverable)	500 mL	1 L HDPE bottle	HNO_3 to pH<2	6 months
Zinc, Copper (dissolved)	500 mL	1 L HDPE bottle	HNO_3 to pH<2	6 months
Hardness	100 mL	100 mL	H_2SO_4 to pH<2	6 months
Turbidity	100 mL or less collected for field measurements			

Analytical Methods

Laboratory analytical methods are shown in Table 4.

Table 4. Analytical methods.

Analyte	Sample Preparation Method	Analytical Method	Method Reporting Limit
Zinc, Copper (total recoverable)	Digested with mixture of nitric and hydrochloric acids	EPA 200.8	5 µg/L
Zinc, Copper (dissolved)	Field filtered	EPA 200.8	1 µg/L
Hardness	--	EPA 200.7	1 mg/L
Turbidity	--	Std Method 2130	0.5 NTU

Turbidity was field-measured with a Hach portable ratio-type turbidimeter, similar to the laboratory model of the same series. The field units have been found to be accurate. Field and laboratory results from paired samples were close to identical (Slope = 1.0281, R^2 = 0.9902) (Lubliner and Golding, 2005).

Data Quality

Manchester Environmental Laboratory prepared written quality assurance reviews on the quality of the metals data for this project. The reviews include an assessment of sample condition on receipt at the laboratory, compliance with holding times, instrument calibration, procedural blanks, laboratory control samples, matrix spike and matrix spike duplicate recoveries, and duplicate sample analyses.

No problems were encountered that compromise the accuracy, validity, or usefulness of the data, with the following exceptions:

- The dissolved zinc concentration of 95 µg/L in sample 344241 was significantly greater than the total concentration of 64.6 µg/L.
- The duplicate relative percent difference (RPD) for sample 394254 for copper collected September 30 – October 1 was greater than acceptance limits. The duplicate value is used in this report.

Laboratory duplicates and field replicates provide estimates of analytical precision and sampling variability. Appendix B shows precision data from laboratory duplicates and field replicates. Also shown are results from blank samples of deionized water used to assess any contamination of samples from transfer or filtering into containers.

Relative percent difference (RPD) is a measure of variability obtained by dividing the difference between two values by their mean, expressed as a percentage. The laboratory method acceptance range for metals results is 0% - 20% RPD. The RPDs for all laboratory duplicates were below 20% with the exceptions of the zinc total recoverable and copper total recoverable for sample lab no. 394254. Those RPDs, 53% and 84%, respectively, appear anomalous and are likely the result of a non-homogenous sample or contamination of the sample in the laboratory (Jones, 2006). For lab no. 394254 samples, the lower duplicate values are consistent with trends in the data and have been adopted to represent actual results.

Field replicates for zinc and copper (total recoverable and dissolved) showed low variability: a mean RPD of 4.5% and a maximum of 10%.

One outlier was identified in the project data. The August 28/29 monitored event showed a dissolved zinc concentration of 95 µg/L for the hour-9 sample (lab no. 05344241 – Appendix A). This is 47% higher than the 64.6 µg/L total recoverable zinc concentration reported for this sample. This is outside the normal variability of metals results. A plot of total recoverable and dissolved concentrations for the storm event also showed the 95 µg/L data point as an evident outlier. The data point is included in parentheses in the data table (Appendix A) but excluded from the graphical plots of the data.

A Quality Assurance (QA) Project Plan was prepared for this project (Golding, 2005). The QA Project Plan specifies that the lowest metals concentrations of interest be at least 10 times lower than the applicable water quality criteria. During this study, the highest blank result for dissolved zinc was 5.6 µg/L, eight times lower than the dissolved zinc water quality criterion of 45 µg/L (for the minimum hardness of 34 mg/L encountered in this study). The highest blank result for dissolved copper was 0.47 µg/L. This meets the data quality objective of at least 10 times lower than the 6.16 µg/L minimum criterion for this study.

The benchmark levels of 117 µg/L total zinc, and 63.9 µg/L total copper, set in the ISGP are well above 10 times the blank results.

Low concentrations of metals were found in the first six hours of sampling before the August storm event. These low concentrations approached those of the transfer blanks (Appendix B).

Results and Discussion

Characteristics of Monitored Storm Events

Three storm events were monitored and samples collected between August and December 2005. All three events were preceded by two weeks or more of no precipitation.

The number of dry days preceding each storm event and the peak streamflow for each event are shown in Table 5.

Table 5. Dry days preceding and peak streamflow during monitored events.

Monitoring Dates (2005)	Dry Days Preceding	Event Peak Streamflow (cfs)
Aug 28-29	37	13
Sept 29-Oct 1	19	23
Dec 19-20	17	9.7

The first storm monitored was the first storm event of the season. It was preceded by 37 days of dry weather from mid-July through August. All events followed 17 or more days of no measurable precipitation. Peak streamflows were relatively low for each storm event, providing an opportunity to compare similar storms with varying days of preceding dry conditions.

Figure 3 is a hydrograph for USGS gage station 12113349, showing daily average streamflow for July 2005 – January 2006. The three monitored events are shown in the figure with their corresponding spikes in streamflow. Days of preceding dry weather appear as flat areas on the hydrograph to the left of each event.

The number and nature of intervening storms between each monitored storm event may have an effect on the nature of the subsequent monitored event. There was a single intervening storm between the August and September/October monitored events, with a maximum daily average of 24 cfs on September 10.

The final monitored storm in December was preceded by two large storms. The first, with a maximum daily average streamflow of 28 cfs, caused streamflow to be elevated for 10 days in late November and early December. The second storm had a maximum daily average of 57 cfs on December 2 with 14 days of elevated streamflow. The final monitored event also proved to be the initial portion of overlapping storms typical of the wet-weather season in western Washington.

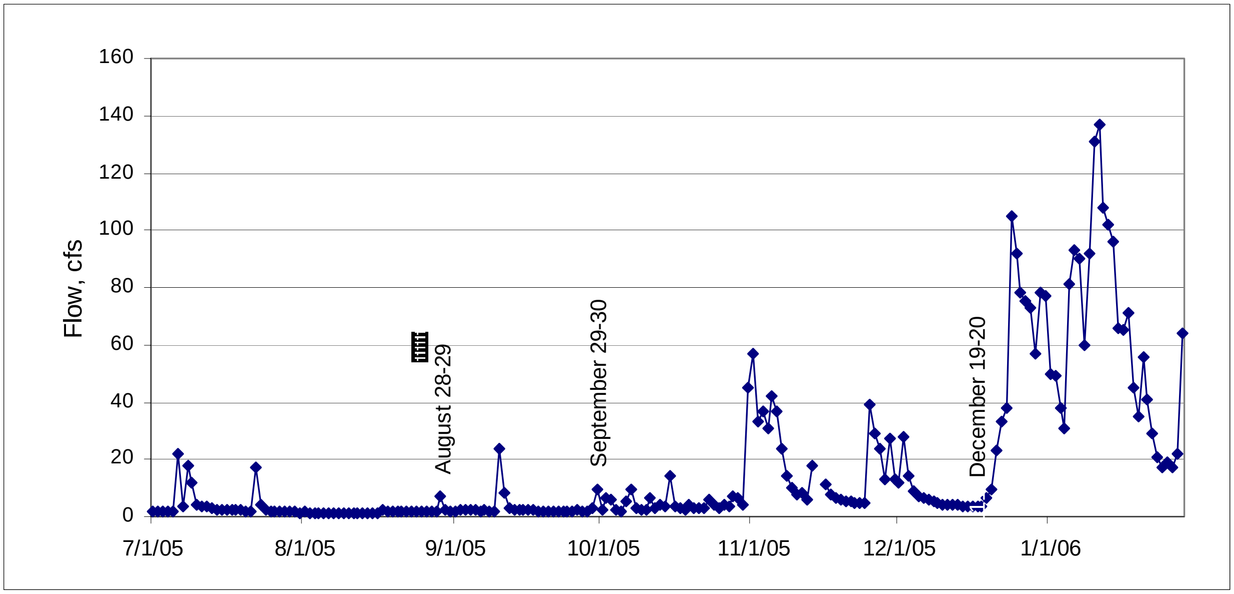


Figure 3. Hydrograph of daily average streamflow, July 2005 – January 2006.

Excursions from Water Quality Standards

The hourly composite samples of this study provided dissolved zinc and copper data to compare directly with acute (one-hour) water quality criteria, as specified in the Water Quality Standards (Ecology, 2003). The initial assumption that worst-case conditions for these metals are during storm events rather than dry conditions was confirmed by results of hour-by-hour time series data, which show low zinc and copper concentrations preceding each storm event.

Acute water quality criteria for dissolved zinc were exceeded on two consecutive hours during the August storm event, and on three consecutive hours during the September/October storm event. Acute water quality criteria for dissolved copper were exceeded on two consecutive hours during the September/October storm event.

Table 6 shows exceedances of acute water quality criteria found in this study. Figures 4 – 6 show them in chart form.

Table 6. Zinc and copper exceedances (µg/L) of acute water quality criteria.

Date (2005)	Zinc (dissolved)			Copper (dissolved)		
	Receiving water	Acute criterion	Hardness (mg/L)	Receiving water	Acute criterion	Hardness (mg/L)
Aug 28 – Aug 29	100	87.5	72.8	--	--	--
	98.5	87.6	72.9			
Sept 29 – Oct 1	75.9	59.4	46.1	10.4	8.2	46.1
	79.3	53.2	40.6	9.4	7.3	40.6
	55.7	49.7	36.9	--	--	--

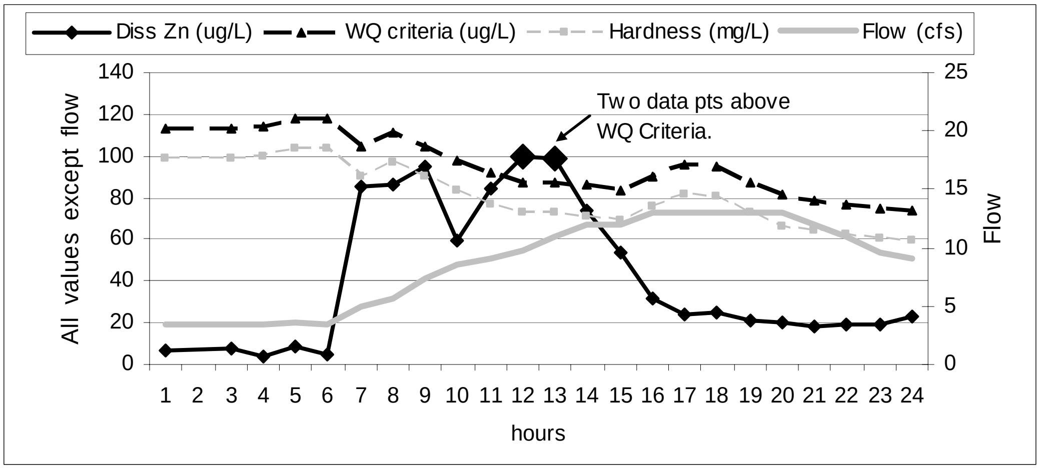


Figure 4. Dissolved zinc concentrations and acute water quality criteria, Aug. 28 - 29.

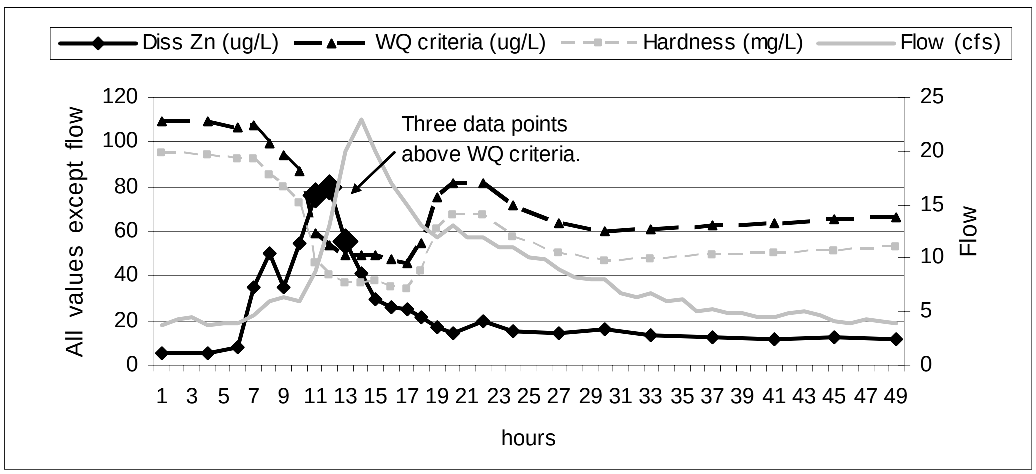


Figure 5. Dissolved zinc concentrations and acute water quality criteria, Sept. 29 - Oct. 1.

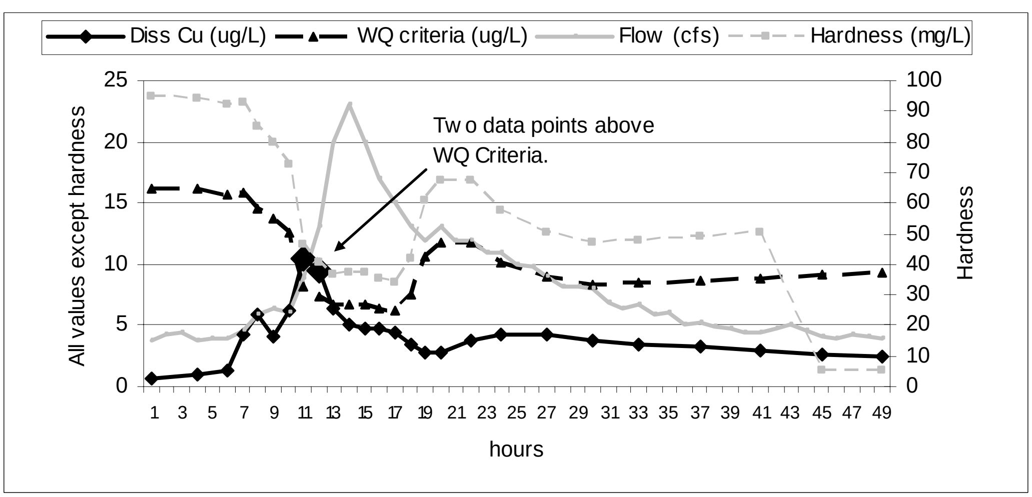


Figure 6. Dissolved copper concentrations and acute water quality criteria, Sept. 29 - Oct. 1.

Figures 4 – 6 show that zinc and copper concentrations in Mill Creek begin to climb as streamflow increases during a storm event. At the same time, water quality criteria, which are dependent on hardness, begin to dip. Where data points on the line representing metals concentrations are higher than the criteria line, there are water quality criteria exceedances. For the storm events of Figures 4 – 6, exceedances occurred before the streamflow peaked. As shown on the figures, the criteria track hardness, which tends to diminish during a storm event as the receiving water is diluted with surface runoff.

Zinc and Copper Time-series Results

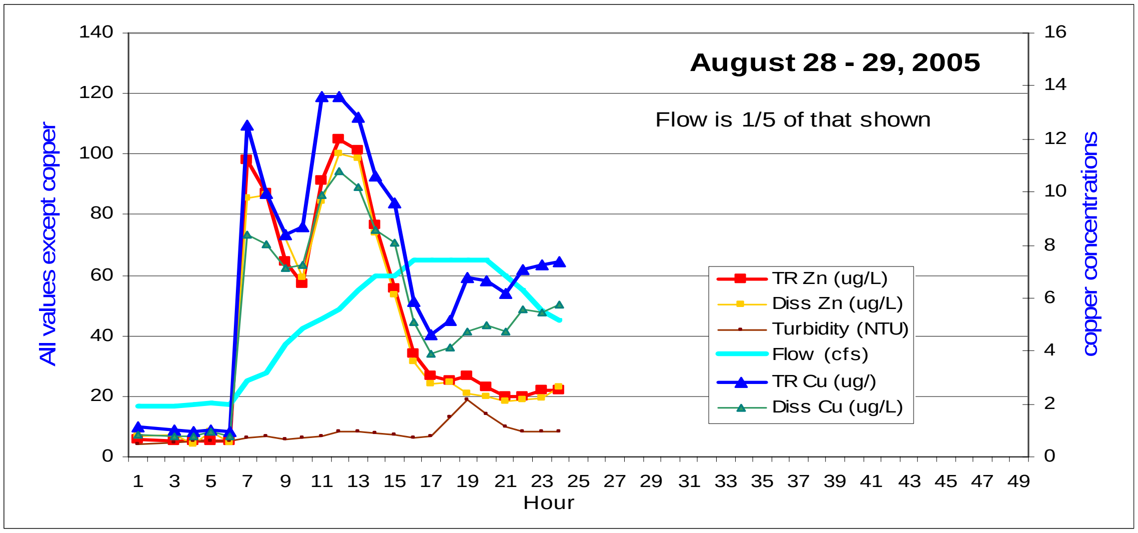
A secondary objective of this study was to produce, for each monitored storm event, a time series of at least 24 hours or longer. Because continuous streamflow is included in the data set, it is possible, among other things, to calculate pollutant loading. Figure 7 shows plots of all data. Data appear in tabular form in Appendix A.

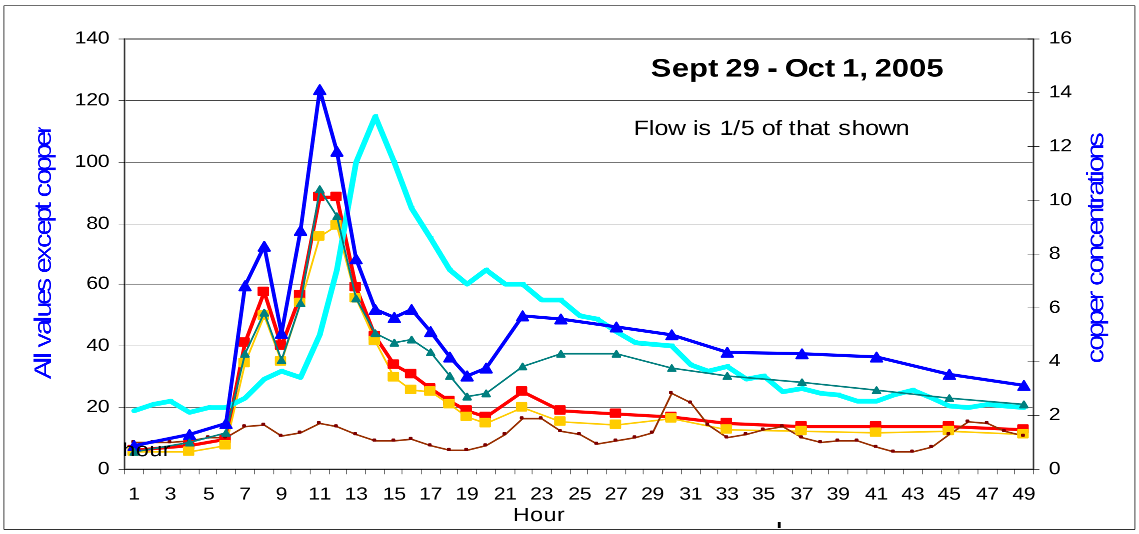
The patterns of the time-series charts for the first and second monitored storm events are similar in appearance, showing dual peaks in metals concentrations preceding maximum streamflow. The chart for the third monitored event, in December, appears markedly different. That event, unlike the other two, was preceded by large storm events (see Figure 3). Its chart shows a simpler pattern with peak streamflow and metals concentrations coinciding in time.

Minimum and maximum metals concentrations observed during the storms are shown in Table 7. Metal concentrations and continuous flow data allow for analyses beyond the scope of this study, including event mean concentrations, which requires a process of defining the onset and end of storm periods.

Table 7. Minimum and maximum zinc and copper concentrations (µg/L).

Storm Event:	Aug 28-29 min/max	Sept 29 / Oct 1 min/max	Dec 19-20 min/max
Zinc			
Total recoverable	5.0 / 105	6.0 / 88.7	19 / 75.9
Dissolved	4.0 / 100	5.7 / 79.3	18.3 / 58.4
Copper			
Total recoverable	0.94 / 13.6	0.89 / 14.1	1.23 / 6.01
Dissolved	0.75 / 10.8	0.67/10.4	0.74 / 3.14





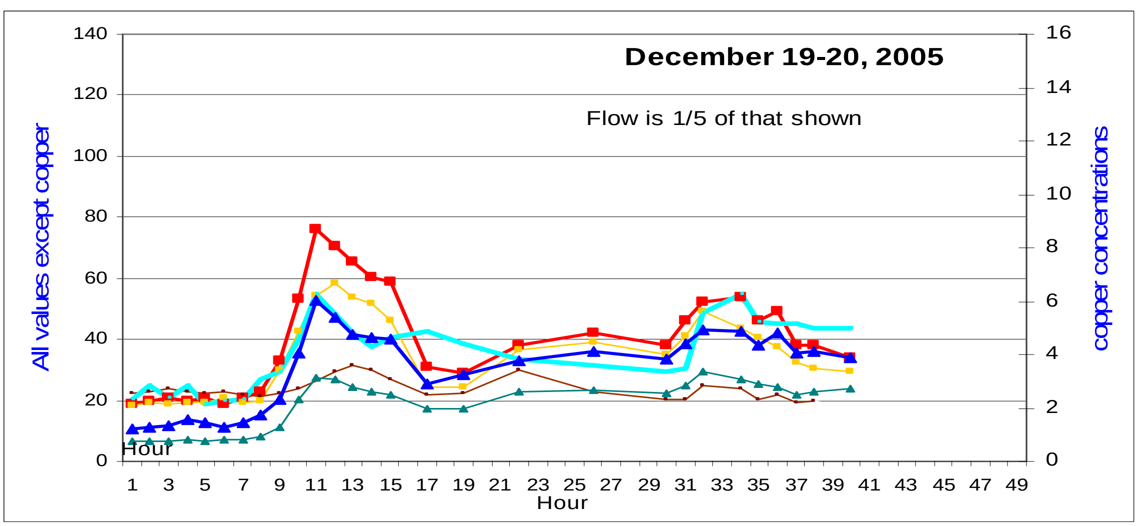


Figure 7. Complete time series of all data collected during the three storm events.

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Mean percentages of metals in the dissolved form for the three monitored events are shown in Table 8. There was a trend toward lower percentages of dissolved copper (higher metals as particulate) as the season progressed. Dissolved zinc showed no clear trend, with the portion in dissolved form near 90%.

Table 8. Mean percentages of total metals in dissolved form.

Storm Event	Zinc	Copper
August 28 – 29	94	79
Sept 29 / Oct 1	88	71
December 19 -20	88	61

Other observed patterns in the data:

- Plots of zinc and copper follow each other closely in shape during all three storm events, peaking together with respect to time.
- Metals concentrations rose quickly during the first two monitored events. The August storm showed the most rapid increase in metals concentrations, with total zinc rising abruptly from 5 µg/L to 98.3 µg/L within the span of one hour.
- Metals concentrations peaked well before peak streamflow during the August monitoring event. The two peaks became closer together during the second monitored storm event, and then coincided during the December event.
- Turbidity appeared to track other parameters closely in the final, monitored storm event in December. The two earlier events appeared to show no relationship between turbidity and other parameters.

Elevated Metals in ISGP Discharges and in Mill Creek

The principal objective of this study was to evaluate the potential to find exceedances of water quality criteria for zinc and copper in receiving waters in industrialized areas.

The finding of zinc and copper exceedances of water quality criteria in creek water suggests that such exceedances may occur in other receiving waters in industrialized areas.

There are indications that the elevated levels of zinc and copper in stormwater discharges from industrial facilities are not only associated with elevated levels of the metals in Mill Creek but are a principal cause of the water quality criteria exceedances in the creek during storm events:

- Industrial stormwater runoff appears to be the source of the majority of runoff into Mill Creek during storm events (Appendix C). With a peak flow of 13 cfs for the August storm event and a baseflow of approximately 4 cfs, (Appendix A), half of the flow in Mill Creek above baseflow can be attributed to runoff from industrial land use.

- The high concentrations of zinc and copper in industrial stormwater discharges to Mill Creek can account for the elevated concentrations in the creek during storm events. The concentrations of zinc in Mill Creek during periods of excursions from criteria were as high as 105 µg/L total zinc (100 µg/L dissolved), compared with industrial stormwater discharges with higher total zinc concentrations: more than 55% exceeding 117 µg/L (benchmark) and 21% exceeding 372 µg/L (action level). For copper, 14.1 µg/L total (10.4 µg/L dissolved) in the creek compares with 21% exceeding 63.9 µg/L (benchmark) and 6% exceeding 149 µg/L (action level).

- Findings from the National Stormwater Quality Database (Pitt et al., 2004) support industrial land use as a major source of zinc and copper in stormwater runoff. A median value of 112 µg/L dissolved zinc from industrial land use is higher than for other land uses evaluated in the study: residential, commercial, freeways, and open space. Three land uses were associated with similar median concentrations of dissolved copper: 8 µg/L industrial, 7.6 µg/L commercial, and 10.9 freeways.

- There are few waterbodies in Washington State for which zinc or copper are included in the 303(d) list of impaired waters (Appendix D – Ecology, 2004). The 2004 Integrated Water Quality Assessment lists only six creeks as impaired for zinc and six creeks for copper (category 5). Mill Creek then, with data from this study comparable to those for 303(d) listed waterbodies, is unusually high in zinc and copper concentrations. This points toward the unusually high density of industrial facilities in the Mill Creek drainage area, with their high concentrations of zinc and copper in stormwater runoff. However, relatively few creeks have undergone a significant level of stormwater sampling, so that the number of creeks warranting listing may be greater than indicated.

Conclusions

Monitoring of three 2005 storm events in Mill Creek showed that acute water quality criteria for zinc were exceeded for two consecutive hours during the first storm event and for three consecutive hours during the second event. Criteria for copper were exceeded for two consecutive hours during the second storm event.

Results of this case study of Mill Creek were consistent with the assumption that worst-case conditions in western Washington receiving waters are found during the initial stages of storm events. Both zinc and copper concentrations and excursions from water quality criteria increased during storm events.

There are indications that the elevated levels of zinc and copper in stormwater discharges from industrial facilities are not only associated with elevated levels of the metals in Mill Creek, but are the principal cause of water quality criteria exceedances in the creek during storm events.

With the onset of each of the three monitored storm events, metals concentrations increased with increasing streamflow. At the same time, hardness and water quality criteria decreased. The overall effect favored exceedances of water quality criteria. It appears that the calcium and magnesium comprising hardness are diluted by stormwater runoff. The lowering of hardness with increases in streamflow is a pattern commonly observed in other western Washington receiving waters.

Graphs representing total and dissolved zinc and copper tracked each other closely over time throughout each storm event.

Dissolved zinc concentrations as a percent of total were fairly uniform, approximately 90% for the three storm events. Dissolved copper concentrations ranged from 61% to 79%.

During the first monitored storm event (in August), zinc and copper concentrations peaked well before peak streamflow. The September/October event saw the gap between the peaks narrow. The December event, unlike the other two, was preceded by considerable rainfall and rises in streamflow in the month before monitoring. During the December event, all peaks for flow, metals concentrations, hardness, and turbidity coincided.

The final monitored event (in December) saw a less rapid rise in metals concentrations and the smallest overall rise compared with the other two monitored events. This supports the assumption that critical pollutant concentrations are found in the early-season, first-flush storm events.

Recommendations

Monitoring for critical metals concentrations in receiving waters should not be limited to dry-weather periods, but instead should take place during storm events. These storm events should include, when possible, first-flush conditions after a period of little or no precipitation.

In general, determination of compliance/non-compliance of a receiving water with Washington State water quality criteria during storm events should be based on acute, one-hour criteria. The inclusion of several sub-samples within each hourly sample would provide a better representation of acute, one-hour conditions than would a single sample per hour.

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Appendices

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Appendix A. Raw Data for August, September/October, and December Monitoring Events

Table A-1. August 28 – 29, 2005 sampling period.

Hour	Lab #	Time	Flow	TR ZN	DISS ZN	TR CU	DISS CU	Hardness	Turbidity
			cfs	µg/L	µg/L	µg/L	µg/L	mg/L	NTU
1	344234	1530	3.4	5.8	6.7	1.16	0.81	98.3	4.1
2									
3	344235	1730	3.4	5.4	7.2	1.03	0.75	98.6	4.5
4	344236	1830	3.5	5.0	4.0	0.94	0.76	100	5.1
5	344237	1930	3.6	5.5	8.4	0.99	0.98	104	5.0
6	344238	2030	3.5	5.0	4.7	0.96	0.78	104	5.0
7	344239	2130	5.0	98.3	85.7	12.5	8.38	90.3	6.4
8	344240	2230	5.6	87.0	86.3	9.92	8.04	96.4	6.6
9	344241	2330	7.4	64.6	(95)	8.38	7.11	89.9	5.7
10	344242	0030	8.5	57.1	59.1	8.69	7.23	83.3	6.2
11	344243	0130	9.1	91.0	84.6	13.6	9.86	76.9	6.7
12	344244	0230	9.8	105.0	100.0	13.6	10.8	72.8	8.2
13	344245	0330	11.0	101.0	98.5	12.8	10.2	72.9	8.2
14	344246	0430	12.0	76.3	74.1	10.6	8.57	71.4	7.7
15	344247	0530	12.0	55.7	53.6	9.61	8.06	69.3	7.3
16	344248	0630	13.0	34.0	31.6	5.86	5.1	75.3	6.3
17	344249	0730	13.0	27.0	24.2	4.59	3.91	81.5	6.9
18	344250	0830	13.0	25.0	24.6	5.14	4.12	80.2	13.1
19	344251	0930	13.0	27.0	20.9	6.78	4.73	72.8	18.9
20	344252	1030	13.0	23.0	19.7	6.64	4.99	66.6	14.3
21	344253	1130	12.0	20.0	18.4	6.15	4.76	64.3	10.1
22	344254	1230	11.0	20.0	19.0	7.07	5.59	62	8.3
23	344255	1330	9.6	22.0	19.5	7.24	5.48	60.8	8.2
24	344256	1430	9.0	22.0	22.9	7.37	5.76	59.7	8.3

TR = total recoverable
DISS = dissolved
ZN = zinc
CU = copper
(95) - data point is excluded as an outlier

Table A-2. September 29 – October 1, 2005 sampling period.

Hour	Lab #	Time	Flow	TR ZN	DISS ZN	TR CU	DISS CU	Hardness	Turbidity
			cfs	μg/L	μg/L	μg/L	μg/L	mg/L	NTU
1	394230	1230	3.8	6.0	5.7	0.89	0.67	94.6	9
2			4.2						8.5
3			4.4						8.6
4	394231	1530	3.7	7.9	5.7	1.32	0.98	94.3	9.2
5			4.0						10.2
6	394232	1730	4.0	10.0	7.8	1.71	1.33	92.1	10.2
7	394233	1830	4.6	41.0	34.6	6.81	4.28	92.5	13.8
8	394234	1930	5.9	57.4	49.8	8.27	5.83	85	14.6
9	394235	2030	6.4	40.0	35.2	5.04	4.06	79.5	10.7
10	394236	2130	6.0	56.8	54.3	8.91	6.18	72.6	11.7
11	394237	2230	8.8	88.7	75.9	14.1	10.4	46.1	14.9
12	394238	2330	13.0	88.4	79.3	11.8	9.4	40.6	13.9
13	394239	0030	20.0	59.3	55.7	7.84	6.35	36.9	11.1
14	394240	0130	23.0	43.0	41.6	5.97	5.07	37.1	9.1
15	394241	0230	20.0	34.0	29.6	5.63	4.69	37.2	9.5
16	394242	0330	17.0	31.0	25.8	5.95	4.82	35.3	9.9
17	394243	0430	15.0	26.0	25.1	5.1	4.35	34.1	7.6
18	394244	0530	13.0	22.0	21.1	4.2	3.48	42.1	6.3
19	394245	0630	12.0	19.0	16.8	3.49	2.7	61.0	6.3
20	394246	0730	13.0	17.0	14.7	3.75	2.83	67.2	7.7
21			12.0						11.4
22	394247	0930	12.0	25.0	20.1	5.72	3.81	67.1	16.5
23			11.0						16.6
24	394248	1130	11.0	19.0	15.6	5.59	4.28	57.2	12.3
25			10.0						11.3
26			9.8						8.4
27	394249	1430	9.0	18.0	14.2	5.32	4.27	50.3	9.5
28			8.2						10.4
29			8.1						11.6
30	394250	1730	8.0	17.0	16.3	5	3.77	46.8	24.7
31			6.8						21.7
32			6.4						14.4
33	394251	2030	6.7	15.0	13.1	4.38	3.46	47.8	10.4
34			5.9						11.5
35			6.1						13
36			5.0						13.7
37	394252	0030	5.3	14.0	12.6	4.32	3.21	49.1	10.2
38			4.9						8.6
39			4.8						9.5
40			4.4						9.4
41	394253	0430	4.4	14.0	11.8	4.16	2.94	50.2	7
42			4.8						5.9
43			5.1						5.7
44			4.6						7.2
45	394254	0830	4.1	14.0	12.4	3.55	2.63	51.4	11.3
46			4.0						15.6
47			4.2						14.9
48			4.1						12.5
49	394255	1230	4.0	13.0	11.2	3.14	2.43	52.4	10.6

DISS – dissolved TR – total recoverable ZN = zinc CU = copper

Table A-3. December 19 – 20, 2005 sampling period.

Hour	Lab #	Time	Flow	TR ZN	DISS ZN	TR CU	DISS CU	Hardness	Turbidity
			cfs	µg/L	µg/L	µg/L	µg/L	mg/L	NTU
1	514281	0030	4.1	19.0	18.3	1.23	0.77	93.7	22.3
2	514282	0130	5.0	20.0	19.1	1.25	0.74	94.8	22.9
3	514283	0230	4.2	21.0	18.7	1.36	0.77	95.3	23.9
4	514284	0330	5.0	20.0	19.4	1.56	0.79	96.1	22.9
5	514285	0430	3.8	21.0	19.3	1.43	0.78	96.7	22.2
6	514286	0530	4.0	19.0	20.7	1.27	0.8	97	23
7	514287	0630	4.1	21.0	19.2	1.44	0.84	96.6	22
8	514288	0730	5.4	23.0	19.9	1.73	0.92	96.2	21.2
9	514289	0830	5.9	33.0	30.0	2.3	1.28	92.1	22.1
10	514290	0930	8.0	53.1	42.6	4.04	2.34	72.1	23.6
11	514291	1030	11.0	75.9	54.1	6.01	3.14	60.6	26.4
12	514292	1130	9.6	70.6	58.4	5.41	3.1	64.1	29.2
13	514293	1230	8.4	65.5	54.0	4.75	2.76	67.7	31.3
14	514294	1330	7.5	60.5	51.5	4.61	2.59	69.6	29.9
15	514295	1430	8.1	58.8	46.4	4.57	2.5	70.9	26.8
16									
17	514296	1600	8.5	31.0	24.1	2.9	1.99	81.6	21.7
18									
19	514297	1800	7.7	29.0	24.1	3.26	1.98	85.8	22.4
20									
21									
22									
23	514298	2100	6.7	38.0	36.4	3.76	2.58	91.2	29.9
24									
25									
26									
27	514299	0100	6.3	42.0	39.0	4.1	2.67	72.9	22.9
28									
29									
30									
31	514300	0500	5.9	38.0	35.0	3.81	2.56	71	20.3
32	514301	0600	6.1	46.0	41.2	4.39	2.85	61.4	20.5
33	514302	0700	9.7	52.5	49.0	4.94	3.34	47.8	24.7
34									
35	514303	0900	11.0	53.6	43.4	4.88	3.06	48.1	23.9
36	514304	1000	9.1	46.0	40.6	4.34	2.87	47.9	20.5
37	514305	1100	9.0	49.0	37.5	4.79	2.81	47.9	21.7
38	514306	1200	9.0	38.0	32.3	4.03	2.52	54.1	19.5
39	514307	1300	8.7	38.0	30.2	4.12	2.63	63.8	19.7
40	514308	1500	8.7	34.0	29.6	3.9	2.73	66.2	17.6

DISS – dissolved
TR – total recoverable
ZN = zinc
CU = copper

Appendix B. Precision Data and Blank Results

Table B-1. Lab duplicates.

Parameter	Sample	Date	Lab Duplicates		
			Sample 1	Sample 2	RPD *
Zinc, TR (µg/L)	MTHBASE	8/28/2005	5.7	6.8	18%
	MTH19	8/29/2005	27	26	4%
	MTH3C	9/29/2005	10	10	0%
	MTH25C	10/1/2005	24	14	53%
	MTH20D	12/20/2005	38	38	0%
	MTH20D	12/20/2005	38	38	0%
	TRNSF	12/19/2005	5.0 U	5.0 U	0%
Zinc, diss (µg/L)	MTHBASE	8/28/2005	6.9	6.1	12%
	MTH24	8/29/05	22.9	21.1	8%
	MTH1C	9/29/2005	5.7	5.2	9%
	MTH21C	9/30/2005	16.3	15.6	4%
	MTH01D	12/19/2005	18.3	18.5	1%
	MTH20D	12/20/2005	35.0	34.7	1%
Copper, TR (µg/L)	MTHBASE	8/28/2005	1.42	1.36	4%
	MTH19	8/29/2005	6.78	6.71	1%
	MTH3C	9/29/2005	1.71	1.70	1%
	MTH25C	10/1/2005	8.66 J	3.55	84%
	MTH20D	12/20/2005	3.81	3.81	0%
	TRNSF	12/19/2005	0.33	0.31	6%
Copper, diss (µg/L)	MTHBASE	8/28/2005	0.78	0.75	4%
	MTH24	8/29/2005	5.76	5.73	5%
	MTH1C	9/29/2005	0.67	0.66	2%
	MTH21C	9/30/2005	3.77	3.71	2%
	MTH01D	12/19/2005	0.77	0.76	1%
	MTH20D	12/20/2005	2.56	2.59	1%
Hardness (mg/L)	MTHBASE	8/28/2005	97.3	98.2	1%
	MTH17	8/29/2005	81.5	81.1	0%
	MTH13C	9/30/2006	35.3	35.2	0%
	MTH06D	12/19/2005	96.7	97.6	1%
	MTH26D	12/20/2005	54.1	54.2	0%

TR –	Total recoverable
Diss –	Dissolved
BASE	Background sample taken 10:00 AM August 28. First sequential sample, MOUTH-1, taken 3:00 PM August 28.
TRNSF	Transfer blank
*	Relative percent difference, RPD is equal to the difference between sample and result divided by the mean of the two values, expressed as a percentage.
U	The analyte was not detected at or above the reported result.
J	The numeric result is an estimate

Table B-2. Field replicates.

Parameter	Sample	Date	Field Replicates		
			Sample 1	Sample 2	RPD
Zinc (µg/L)					
Total recoverable	MTHBASE	8/28/2005	5.7	5.7	0%
Dissolved	MTHBASE	8/28/2005	6.9	7.3	3%
Copper (µg/L)					
Total recoverable	MTHBASE	8/28/2005	1.42	1.28	10%
Dissolved	MTHBASE	8/28/2005	0.78	0.82	5%
Hardness (mg/L)	MTHBASE	8/28/2005	97.3	98.2	1%

Table B-3. Field blanks.

Parameter	Field Blanks		
	Sample Type	Date	Result
Zinc (µg/L)			
Total recoverable	Transfer Blank	9/28/2005	5.0 U
		12/19/2005	5.0 U
Dissolved	Filter Blank	8/27/2005	3.3
		9/28/2005	5.6
Copper (µg/L)			
Total recoverable	Transfer Blank	9/28/2005	0.53
		12/19/2005	0.33
Dissolved	Filter Blank	8/27/2005	0.41
		9/28/2005	0.47

U The analyte was not detected at or above the reported result.

Table B-4. Mill Creek samples just prior to the August storm event.
(compare with blank results above)

Sample	Zinc (µg/L)		Copper (µg/L)	
	TR	diss	TR	diss
1530	5.8	6.7	1.16	0.81
1730	5.4	6.7 7.2	1.03	0.75
1830	5	4	0.94	0.76
1930	5.5	8.4	0.99	0.98
2030	5	4.7	0.96	0.78

TR Total recoverable
Diss Dissolved

Appendix C. Estimated Percentages of Total Runoff to Mill Creek by Land Use

From calculations shown in the following tables, an estimated 53% of runoff into Mill Creek is from industrial land use.

Table C-1. Percentage of impervious/pervious surface in the Mill Creek drainage by land use.*

Land Use	% Area Impervious Surface	% Area Pervious Surface
Commercial and Industrial	90	10
Suburban (4 units/acre)	35	65
Vegetated	0	100

*From Booth and Jackson (1997)

Table C-2. Percentage of runoff in the Mill Creek drainage area by surface type.*

Land Surface	% Runoff
Impervious (parking lot, roofs, etc.)	98
Lawn, good condition	68
Pasture, untended land, good condition (ground cover > 75%)	39

* From 2005 Stormwater Management Manual for Western Washington; Table 2.2 *Runoff Curve Numbers for Selected Agricultural, Suburban, and Urban Areas* (Ecology, 2005). Selection of hydrologic soils group A based on alluvium overlying outwash soils (Jones, 1999).

Table C-3. Percentage of runoff in the Mill Creek drainage area by land use.

Land Use	% of Drainage Area	% of Rainfall as Runoff	% of Runoff (normalized to 100% total)
Industrial	44	90	53
Commercial	9	90	11
Residential	25	78.5	25
Vegetated	22	39	11

Example calculation of % of rainfall as runoff for residential land use, Table C-3:

1. % of rainfall as runoff by land use = sum of runoff from pervious and impervious surfaces.
2. Residential: (0.35 impervious) (.98 runoff from impervious) + (.65 pervious) (.68 runoff from lawn) = 78.5% rainfall as runoff with residential land use.

Appendix D. Section 303(d) List of Impaired Waterbodies for Zinc and Copper

The 2004 Integrated Water Quality Assessment lists the following category 5 waterbodies. Category 5 represents the state's 303(d) list of impaired waters.

Table D-1. Zinc – category 5 listings.

Listing ID	Category	WRIA	Waterbody Name
41773	5	1	Baker Creek
41775	5	1	Baker Creek
9106	5	1	Fever Creek
41772	5	1	Squalicum Creek
41776	5	1	Squalicum Creek
41777	5	1	Toad Lake Creek
42308	5	9	Des Moines Creek
42341	5	9	Massey Creek

Table D-2. Copper – category 5 listings.

Listing ID	Category	WRIA	Waterbody Name
9101	5	1	Fever Creek
42309	5	9	Des Moines Creek
42352	5	9	Des Moines Creek, East Tributary
13815	5	9	Hill (Mill) Creek
42342	5	9	Massey Creek
42348	5	9	Massey Creek
42320	5	9	McSorley Creek
13839	5	9	Newaukum Creek
13765	5	9	Newaukum Creek

WRIA – Water Resource Inventory Area