Contaminant Concentrations in Storm Water Entering the Sinclair/Dyes Inlet Subasin of the Puget Sound, USA During Storm Event and Baseflow Conditions

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Introduction

The Sinclair and Dyes Inlet watershed is located on the west side of Puget Sound in Kitsap County, Washington, U.S.A. (Figure 1). Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF), U.S. Environmental Protection Agency (USEPA), the Washington State Department of Ecology (WA-DOE), Kitsap County, City of Bremerton, City of Bainbridge Island, City of Port Orchard, the Suquamish Tribe, and other stakeholders have joined in a cooperative effort to evaluate water-quality conditions in the Sinclair-Dyes Inlet watershed and correct identified problems. A major focus of this project, known as Project ENVVEST, is to develop Water Quality Improvement Projects (also known as Total Maximum Daily Loads – TMDLs) for constituents listed on the 303(d) list within the Sinclair and Dyes Inlet watershed (Johnston 2004). Segments within this watershed were listed on the State of Washington's 1998 303(d) list due to fecal coliform contamination in surface waters, metals in sediment and fish tissue, and organics in sediment and fish tissue (WA-DOE 2003). Stormwater loading was identified by ENVVEST as one potential source of sediment contamination that lacked sufficient data for the contaminant mass balance calculations conducted for the Sinclair-Dyes Inlet watershed. This paper summarizes the results of contaminant concentrations measured in representative streams and outfalls discharging into Sinclair and Dyes Inlets during 18 storm events and wet/dry baseflow conditions between November 2002 and May 2005. This paper serves as a portion of the report entitled, "Surface and Stormwater Quality Assessment for Sinclair and Dyes Inlet, Washington" (Brandenberger *et al.* 2007).

Event Sampling

From summer 2001 to summer 2005 sampling (TEC 2004, Johnston et al. 2005) was conducted to characterize water quality conditions in streams and stormwater outfalls that were representative of the land use and land cover (LULC) within the watershed during baseflow and storm event conditions. Stream and storm water samples were analyzed for alkalinity; hardness; total solids (TS); total suspended solids (TSS); total organic carbon (TOC); total inorganic nitrogen (TIN); total Kjeldahl nitrogen (TKN); total phosphorus (TP); total aluminum (Al); total arsenic (As); dissolved and total silver (Ag), cadmium

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(Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn); polycyclic aromatic hydrocarbons (PAH) consisting of xx low molecular weight (LPAH), xx high molecular weight (HPAH) and 18 polychlorinated biphenyls (PCB) congeners. Baseflow water quality conditions were determined for representative marine stations, streams, and storm water outfalls (Figure 1) during summer dry season baseflow (DSBF: May thru October) and winter wet season baseflow (WSBF: November thru April) in 2001 and WSBF in 2005. DSBF contaminant concentrations were determined as the average of three consecutive days of grab sample collection; while WSBF included grab sample collection plus six hour time-composite samples at selected streams. Flow monitoring stations and area velocity flow meters were used to characterize stream flow and storm driven flow conditions within the Sinclair-Dyes Inlet watershed. Figure 2 shows the typical stream flow patterns for the study area, which typify the “wet” and “dry” seasons of the Pacific Northwest. Since there are many days in the wet season with measurable precipitation not classified as a storm event, samples were collected 24, 48, and 72 hours following a large storm event to determine the length of time required for streams to return to WSBF conditions. The results showed that streams returned to WSBF conditions approximately 72 hours following a storm event.

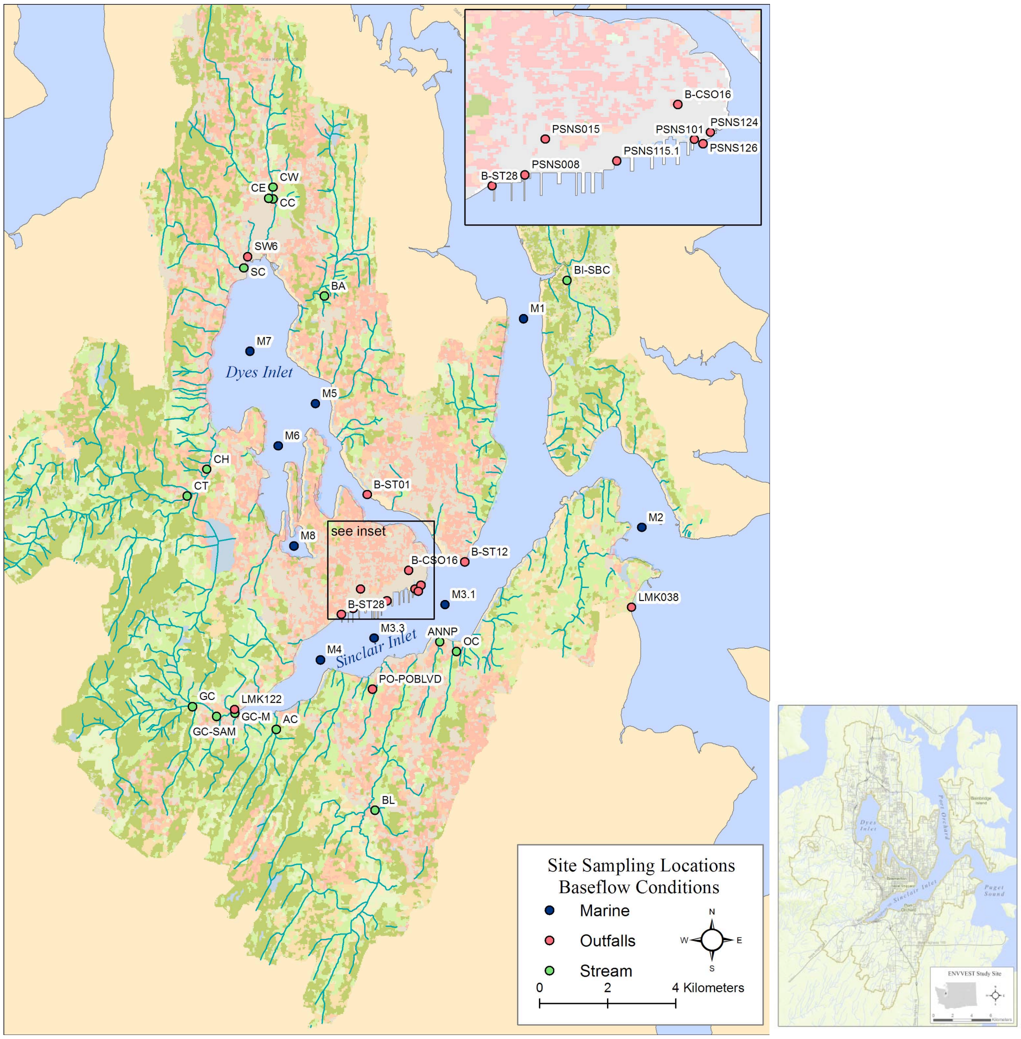

Figure 1 Sinclair-Dyes Inlet Watershed Study Area with Sampling Locations for Streams, Outfalls, and Marine Stations

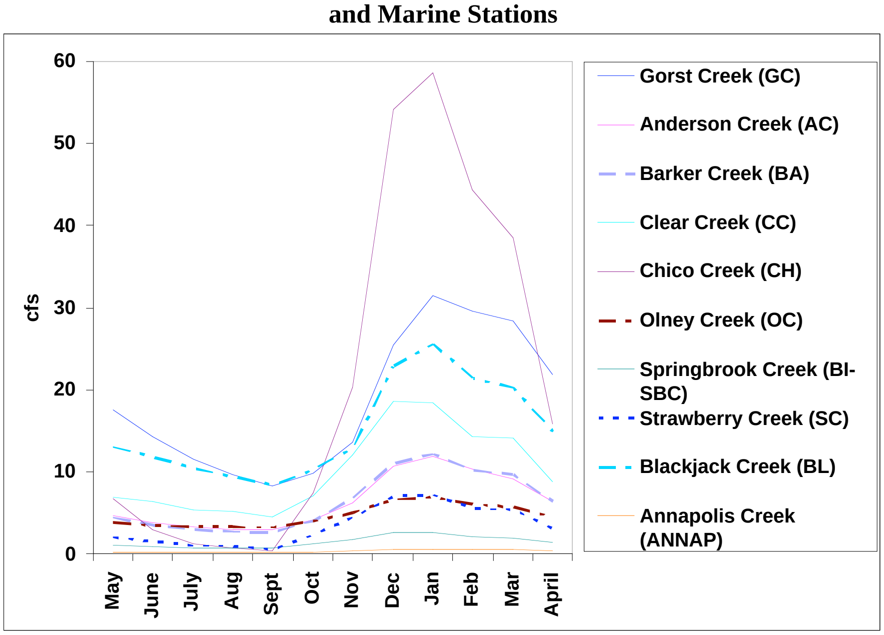

Figure 2 Average Monthly Stream Flow Data for Major Streams in Sinclair-Dyes Inlet

Eighteen storm events were sampled at representative locations in streams, outfalls, and marine waters (Figure 1). Storms were classified based on the total event rainfall as small (0.11-0.5 inches), medium (< 1.0 inch), medium-large (< 2 inches), or large (> 2 inches) (Figure 3a). The antecedent dry period (ADP) ranged from 1-22 days (Figure 3b). The distribution of storms sampled was representative of both the historic rainfall patterns and precipitation that occurred during the study period (WY 2003-2005) based on precipitation analyses conducted by Halkola (2004 and 2006).

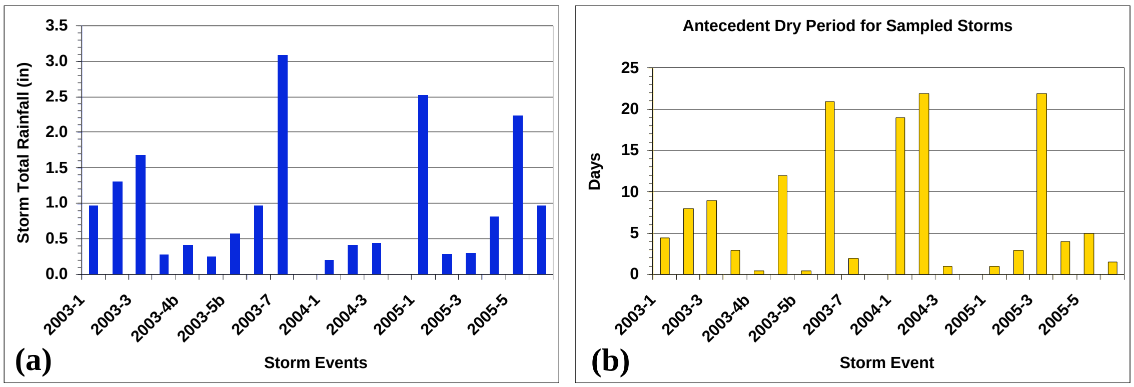

Figure 3   (a) Total Storm Event Rainfall and (b) Antecedent Dry Period for the Storms Sampled

Storm-event sampling was conducted over a three-year period during the winter storm seasons of 2003, 2004, and 2005. The following stations were sampled in each year - in 2003 nine storm events at 11 stream stations; in 2004 three storm events at 1 stream, 15 storm water outfall, 11 marine, and 2 wastewater treatment plant (WWTP) outfalls; and the 2005 task sampled seven storm events at 12 stream, 12 storm water outfall, 4 highway runoff, 21 marine, and 2 WWTP stations. Additional information on field sampling is available in Brandenberger (2007). Stormwater samples were collected using automated samplers (ISCO Model 6700), wherever possible, to generate time-composites for streams and flow-composites for outfalls. If autosamplers were not available, grab samples were collected during three periods of the storm (first hour, anticipated peak, and tailing). Automated samplers were programmed to collect 140 mL aliquots every 15 minutes at streams and 95 mL aliquots every 5 minutes at outfalls. These flow rates filled a 3.8 L (1 gallon) glass interval jar in six hours for streams and three hours for outfalls to generate a time-paced composite sample of a discrete interval of the storm (Figure 4).

Methods

The interval sample jars (see Figure 4) were stored at 4°C and delivered to the laboratory for subsampling and compositing. At the laboratory, interval samples from streams were composited using equal weighting of the time-composite samples (USEPA 1992). Due to the flashy nature of outfall drainage basins and the potential for tidal intrusion, data from *in situ* multi-probe sensors (temperature, conductivity [salinity], turbidity and pH) was coupled with storm flow data to generate a *post hoc* flow-weighted storm composite (EMC sample in Figure 4).

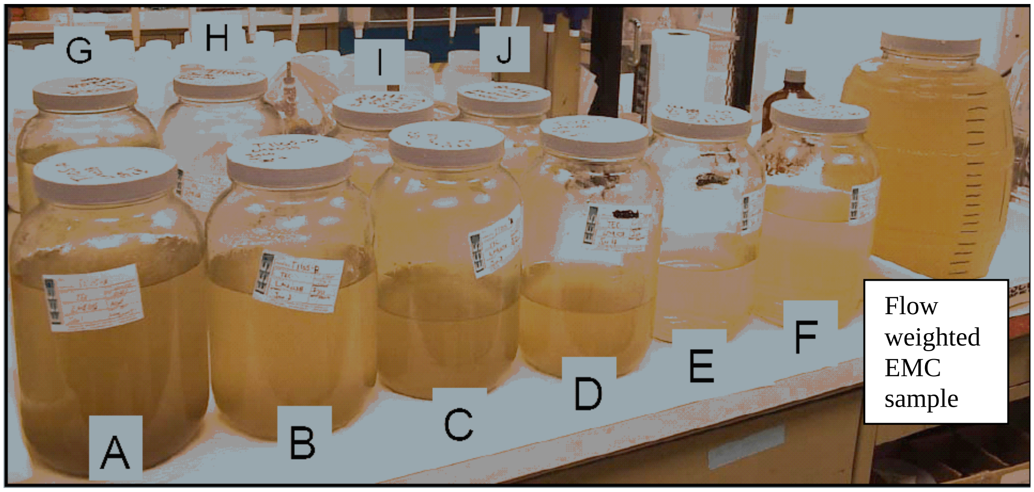

Figure 4 Time-Paced Interval Jars (A thru J) and the Flow Weighted Composite (EMC sample) from Outfall LMK038 Manchester, Each Jar Represents a 3-hour Interval of the Storm

Baseflow samples and storm composites were analyzed for metal and organic contaminants and nutrients to determine event mean concentrations (EMCs). Samples were also analyzed for Al, TSS, TOC, and dissolved organic carbon (DOC) to examine relationships with particulate matter and organic carbon.

All equipment and handling protocols both in the field and laboratory were based on observing ultra-clean techniques for water sample collection following United States Environmental Protection Agency (USEPA) Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. Field blanks were collected to evaluate the potential contamination of the samples during collection, transport, and processing at the laboratory. Half of each sample for metals chemistry was filtered through a 0.45_m pre-cleaned cellulose nitrate filter in a Class 100 clean bench to produce the "dissolved" fraction. USEPA methods or National Oceanic and Atmospheric Administration (NOAA) Status and Trends Methods (NOAA 1998) were used or adapted to enhance analytical performance for all contaminants. A detailed description of all analytical methods is provided in TEC 2004, Johnston et al. 2005, and Brandenberger *et al.* (2007).

Contaminant EMCs and Storm Size

The median EMCs for each of the parameters measured are listed in Table 1 for streams and Table 2 for outfalls (excluding WWTP; available in Brandenberger *et al.* (2007)). EMCs for Cu (Figure 5), Pb, Zn, and Hg show an increasing trend with storm size for streams, but a decreasing trend with storm size for outfalls. In addition, the small storm events in outfalls had the highest degree of variability.

Table 1 Median EMCs for Streams during Baseflow and Storm Conditions of Varying Size

Analytical Parameters	DSBF Median	WSBF Median	Small Storms	Medium Storms	Medium-Large Storms	Large Storms
PHYSIO-CHEMICAL (mg/L)						
Alkalinity	64	40	40	40	36	26

Analytical Parameters	DSBF Median	WSBF Median	Small Storms	Medium Storms	Medium-Large Storms	Large Storms
Hardness	69	41	49	42	39	38
TS	132	88	94	118	124	147
TSS	3	6.0	13	22	26	90
TOC	1.8	6.2	3.7	8.4	8.0	7.4
TIN	0.66	0.60	0.52	0.63	0.63	0.73
TKN	0.35	0.30	0.40	0.60	0.60	0.70
Total P	0.04	0.04	0.06	0.08	0.09	0.11
METALS (_g/L, except Hg ng/L)						
Total Al	68	231	258	694	712	1636
Total As	0.84	1.2	0.66	1.2	1.3	1.5
Total Cd	< 0.01	0.013	0.096	0.085	0.27	1.3
Dissolved Cd	< 0.01	0.012	0.048	0.028	0.12	0.38
Total Cr	0.92	2.0	2.1	3.0	3.3	5.5
Total Cu	0.37	0.96	1.7	2.5	2.6	4.7
Dissolved Cu	0.21	0.68	0.77	0.88	1.2	1.4
Total Pb	0.095	0.24	0.41	0.89	1.0	1.5
Dissolved Pb	0.030	0.066	0.076	0.14	0.14	0.14
Total Ag	0.010	< 0.010	< 0.010	< 0.010	< 0.010	0.016
Dissolved Ag	0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Zn	1.5	4.1	4.0	8.2	11	11
Dissolved Zn	1.0	2.8	2.6	3.4	4.9	3.6
Total Hg (ng/L)	1.2	3.7	4.0	6.8	7.6	11
ORGANICS (ng/L)						
Sum Total PAH	306	27	43	64	42	31
Total LPAH	21	12	17	34	20	13
Total HPAH	181	14	21	20	20	21
Total PCB	2.6	2.0	2.0	2.0	2.0	2.0

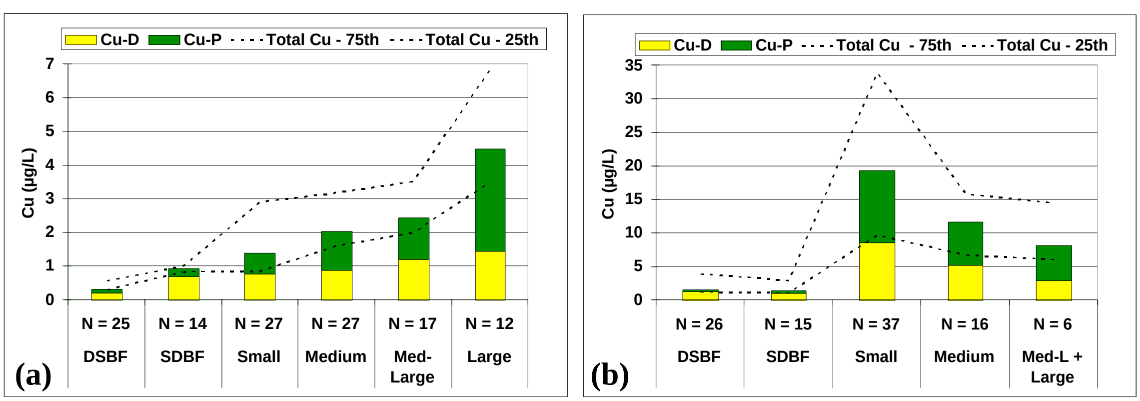

Figure 5 Median EMC in (a) Streams and (b) Outfalls for Dissolved Cu (Cu-D) and Particulate Cu (Cu-P) - the Top of Each Column Represents the Total Cu

Table 2 Median EMCs for Industrial and Urban Outfalls during Baseflow and Storm Conditions

Analytical Parameters	DSBF Median	WSBF Median	Small Storms	Medium Storms	Medium-Large + Large Storms
PHYSIO-CHEMICAL (mg/L)					
Alkalinity	74	53	31	21	20
Hardness	84	58	44	29	29
TS	157	106	154	89	108
TSS	3	2.5	33	31	71
TOC	3.8	4.5	7.6	5.9	6.7
TIN	--	0.83	0.52	0.35	0.53
TKN	--	0.3	1	1	1
Total P	--	0.07	0.21	0.12	0.12
METALS (_g/L, except Hg ng/L)					
Total Al	60	136	797	787	1503
Total As	0.72	1.3	1.6	1.3	0.96
Total Cd	0.018	0.022	0.25	0.27	0.25
Dissolved Cd	0.010	0.021	0.11	0.091	0.093
Total Cr	0.91	2.3	3.9	3.3	4.5
Total Cu	1.8	1.6	20	12	10
Dissolved Cu	1.3	1.1	8.6	5.2	3.0
Total Pb	0.45	0.30	10	9.9	8.3
Dissolved Pb	0.10	0.11	0.72	0.35	0.26
Total Ag	0.013	< 0.010	0.045	0.019	0.012
Dissolved Ag	0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Zn	6.9	12	84	65	50
Dissolved Zn	5.7	9.3	46	30	12
Total Hg (ng/L)	1.9	2.5	17	11	10
ORGANICS (ng/L)					
Sum Total PAH	292	33	163	671	318
Total LPAH	91	12	111	82	110
Total HPAH	191	14	73	608	200
Total PCB	3.2	2.6	2.3	2.4	2.4

The EMCs for PAHs are grouped into LPAH (petrogenically derived) and HPAH (pyrogenically derived), which are summed to represent total PAHs. On average, the total PAH concentrations are dominated by the HPAH fraction with DSBF concentrations among the highest of both streams and outfalls (Figure 6). Unlike metals, PAHs did not show a strong relationship with storm size.

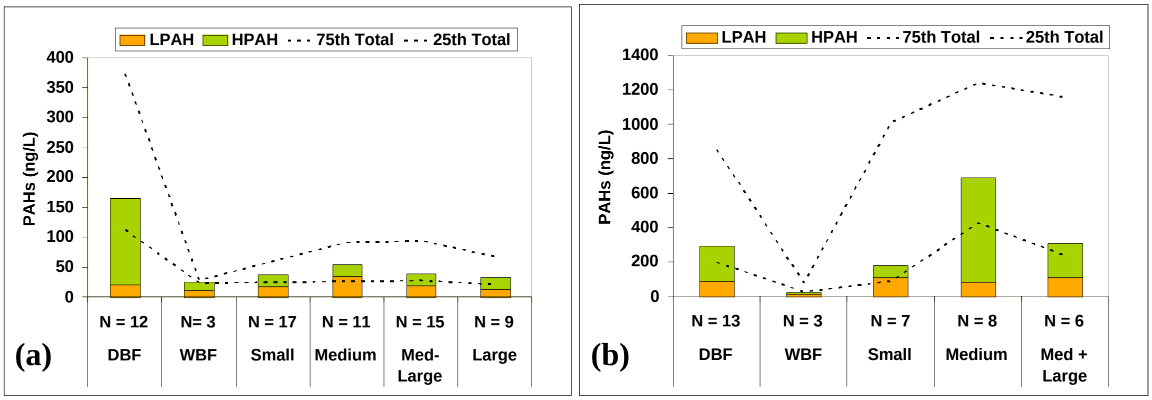

Figure 6 Median EMCs in (a) Streams and (b) Outfalls for LPAH and HPAH - Top of Each Column Represents the Total PAH

Methods Discussion

Collection methods for stormwater are critical to allow comparison of results. Grab sampling methods may not adequately capture all aspects of the storm event resulting in the over/under estimation of the EMC. Figure 7 illustrates the total Cu concentrations in time-paced composites for each interval (green-Figure 7a) and the calculated EMC (orange) for a large storm on Anderson Creek. Precipitation is recorded in blue and turbidity (black) throughout the storm and Figure 7b shows total Cu concentrations in each grab sample along with turbidity in black. Other studies (Roa-Espinosa and Bannerman 1995; Burton and Pitt 2002; Novotny 2003) have shown the method of sampling (i.e. individual grab samples *vs.* automated samplers with flow-weight compositing) and timing (i.e. first hour of the storm *vs.* entire storm) can have a significant influence on stormwater quality monitoring results. In general, the accuracy and reproducibility of composite samples tends to be good, while these attributes for grab samples tends to be poor (Pitt et al. 2004).

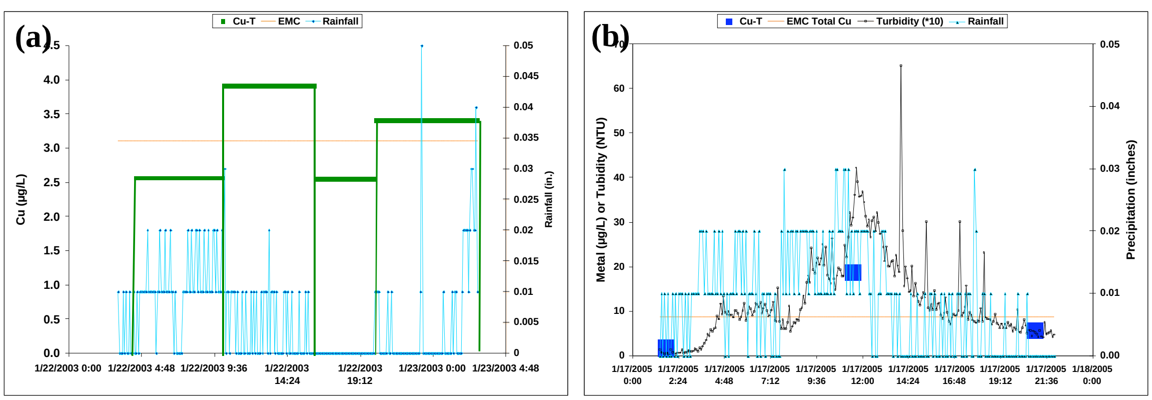

Figure 7 Comparison of Total Cu (a) in Time-Paced Composites for each Interval of the Storm (green) and (b) in each Grab Sample with Calculated EMCs in Orange

Conclusions

The results showed that EMCs for outfalls were often five times higher than streams for metals and 24 times higher for PAHs; however, calculated loadings from outfalls were lower than streams due to the greater volumes discharged from streams. EMCs for total

Cu, Pb, Zn, and Hg in streams were positively correlated with storm size, but an inverse relationship for outfalls was found suggesting a dilution effect with larger storms. The data were used to develop statistical estimates of contaminant levels in streams and outfalls as a function of upstream land use and storm intensity reported in Brandenberger *et al.* (2007).

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