

**COPPER SPECIATION IN HIGHWAY
STORMWATER RUNOFF AS RELATED
TO BIOAVAILABILITY AND TOXICITY
TO ESA-LISTED SALMON**

Final Report

SPR 663



Oregon Department of Transportation

**COPPER SPECIATION IN HIGHWAY STORMWATER
RUNOFF AS RELATED TO BIOAVAILABILITY AND
TOXICITY TO ESA-LISTED SALMON**

SPR 663

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16. Abstract The objectives of this study were to 1) identify the effects of site location, storm hydrology, and water quality parameters on the concentration of dissolved copper ($\text{Cu}^{2+}_{\text{diss}}$) in Oregon highway runoff; 2) establish an analytical technique suitable for the determination of copper speciation in highway stormwater runoff; 3) compare analytically determined free ionic copper ($\text{Cu}^{2+}_{\text{free}}$) concentrations in highway stormwater runoff with modeled concentrations; and 4) develop a qualitative understanding of where and when copper toxicity has the most potential to be problematic for receiving waters. In this study, stormwater runoff from an urban high annual average daily traffic(AADT) site had consistently higher event mean concentrations of measured $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$ than the non-urban sites with lower AADT. First flush samples displayed consistently higher concentrations of both $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. A modified Competitive Ligand Exchange-Cathodic Stripping Voltammetry (CLE-ACSV) technique utilizing salicylaldoxime as an added ligand can be used to determine the speciation of copper in highway stormwater runoff. Analytical results from composite stormwater samples suggest that dissolved copper in highway stormwater runoff is largely complexed by organic matter (typically > 99.9%), and that very little of the copper in stormwater is bioavailable; the concentrations of $\text{Cu}^{2+}_{\text{free}}$ were generally several orders of magnitudes below levels found to inhibit olfaction in Endangered Species Act listed fish species. Elevated $\text{Cu}^{2+}_{\text{diss}}$ levels proved to be the greatest indicator of high $\text{Cu}^{2+}_{\text{free}}$ concentrations. Urban sites with AADT and first flush samples characterized by elevated concentrations of $\text{Cu}^{2+}_{\text{diss}}$ are of the greatest concern with respect to elevated free ionic copper concentrations. Available dissolved organic matter models in Visual MINTEQ overestimate $\text{Cu}^{2+}_{\text{free}}$ concentrations when compared to analytically determined $\text{Cu}^{2+}_{\text{free}}$ concentrations. This imparts a conservatism that makes these models potentially useful for regulatory purposes.					
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SI* (MODERN METRIC) CONVERSION FACTORS

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Symbol When You Know Multiply By To Find Symbol

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LENGTH

in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km

AREA

in ²	square inches	645.2	millimeters squared	mm ²
ft ²	square feet	0.093	meters squared	m ²
yd ²	square yards	0.836	meters squared	m ²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	kilometers squared	km ²

VOLUME

fl oz	fluid ounces	29.57	milliliters	ml
gal	gallons	3.785	liters	L
ft ³	cubic feet	0.028	meters cubed	m ³
yd ³	cubic yards	0.765	meters cubed	m ³

NOTE: Volumes greater than 1000 L shall be shown in m³.

MASS

oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

TEMPERATURE (exact)

°F	Fahrenheit	(F-32)/1.8	Celsius	°C
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LENGTH

mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi

AREA

mm ²	millimeters squared	0.0016	square inches	in ²
m ²	meters squared	10.764	square feet	ft ²
m ²	meters squared	1.196	square yards	yd ²
ha	hectares	2.47	acres	ac
km ²	kilometers squared	0.386	square miles	mi ²

VOLUME

ml	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m ³	meters cubed	35.315	cubic feet	ft ³
m ³	meters cubed	1.308	cubic yards	yd ³

MASS

g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T

TEMPERATURE (exact)

°C	Celsius	1.8C+32	Fahrenheit	°F
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*SI is the symbol for the International System of Measurement

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COPPER SPECIATION IN HIGHWAY STORMWATER RUNOFF AS RELATED TO BIOAVAILABILITY AND TOXICITY TO ESA-LISTED SALMON

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GLOSSARY OF TERMS

$\text{Cu}^{2+}_{\text{diss}}$	Dissolved copper
ADP	Antecedent Dry Period
AADT	Annual Average Daily Traffic
ANOVA	Analysis of Variance
ASV	Anodic Stripping Voltammetry
BLM	Biotic Ligand Model
CI	Confidence Interval
CLE-ACSV	Competitive Ligand Exchange-Cathodic Stripping Voltammetry
Complex	A compound consisting of a metal and nonmetal (ligand) molecule
$\text{Cu}^{2+}_{\text{free}}$	Copper ion not bound to any ligand, bioavailable form
DDI	Ultrapure Distilled De-Ionized water
DI	Laboratory grade De-Ionized water
DGT	Diffusive Gradient in Thin Films
DMT	Donnan Membrane Technique
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EDTA	Ethylenediaminetetraacetic acid
EMC	Event Mean Concentration
EPA	Environmental Protection Agency
ESA	Endangered Species Act
FIAM	Free Ion Activity Model
GIME	Gel Integrated Microelectrodes
HMDE	Hanging Mercury Drop Electrode
IC	Ion Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISE	Ion Selective Electrode
K'_{CuL}	Conditional Stability Constant for Cu-(organic) ligand complex
Ligand	A molecule, ion, or compound that is bonded to a metal atom
L_T	Organic ligand concentration
NICA-Donnan	Humic model based on the combination of the Non-Ideal Competitive Adsorption and Donnan humic models
NMFS	National Marine Fisheries Services
NOM	Natural Organic Matter
NURF	National Urban Runoff Program
ODOT	Oregon Department of Transportation
PLM	Permeation Liquid Membranes
S	Sensitivity (slope) of CLE-ACSV method
SA	Salicylaldoxime (added ligand used in CLE-ACSV in this study)
SCP	Stripping Chronopotentiometry

SHM	Stockholm Humic Model
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
UV	Ultraviolet

1.0 INTRODUCTION

Recent research has shown that very low concentrations of dissolved copper can inhibit the olfactory system of salmon listed as threatened and endangered under the U.S. Endangered Species Act (ESA). Highway stormwater runoff is a source of copper to surface waters inhabited by ESA-listed species. Informed by this research, the National Marine Fisheries Service (NMFS) is more likely to determine in their Biological Opinions (permits issued as part of the consultations performed under Section 7 of the ESA) that transportation projects are “Likely to Adversely Affect” the ESA-listed fish. The delivery of transportation projects is tied to these consultations and Biological Opinions; project timelines can be altered and costly stormwater treatment systems may be required. In natural waters, only a fraction of the dissolved copper (consisting primarily of ionic and weakly complexed species) is bioavailable and toxic to aquatic species. At present, it is unclear how the total dissolved copper is partitioned between ionic and complexed forms in highway stormwater runoff and how that influences copper toxicity.

The overall objective of this study was to develop a fundamental framework for estimating the likely impact of copper in highway stormwater runoff that discharges to surface receiving waters inhabited by ESA-listed fish species in the State of Oregon. This guidance will allow ODOT to predict when, where, and to what extent copper toxicity is likely to be a problem and will inform NMFS in their assessment of the risks associated with transportation projects. Measurement of copper speciation and the concentrations of other constituents that influence copper toxicity are keys to this analysis and therefore were the focus of this work.

1.1 OBJECTIVES

The primary objectives of this work were as follows:

- 1) Identify the effects of site location, storm hydrology, and water quality parameters on the concentration of dissolved copper in Oregon highway runoff;
- 2) Develop an analytical technique for the determination of copper speciation in highway stormwater runoff;
- 3) Compare analytically determined free ionic copper concentrations in highway stormwater runoff with modeled concentrations; and
- 4) Develop a qualitative understanding of where and when copper toxicity has the most potential to be problematic.

1.2 APPROACH

The foundation of this work was an extensive stormwater sampling effort. Composite stormwater samples were collected from four diverse sites in Oregon. First flush and flow-weighted samples were collected from one site in Corvallis to examine variability within individual storms. All composite and first flush samples were analyzed for an extensive array of constituents. Other grab and selected flow-weighted samples were analyzed for trace metals and dissolved organic carbon (DOC), at a minimum. Storm data was collected throughout each sampled storm.

Objective 1 was achieved through statistical analyses of highway runoff samples gathered during the sampling effort. These analyses were aimed at identifying significant differences in copper concentrations between different sites and sample types, as well as determining important variables controlling or correlating with copper concentrations. Objective 2 was accomplished through the development of a competitive ligand exchange–adsorptive cathodic stripping voltammetry technique suitable for use in stormwaters. The method was then used to determine the free ionic copper concentration in stormwater samples. Objective 3 was completed through chemical equilibrium modeling of each stormwater sample using three dissolved organic matter (DOM) models available in Visual MINTEQ (Gaussian, Non Ideal Competitive Adsorption-Donnan, and Stockholm Humic Model) and subsequently comparing the modeled and experimental results. For Objective 4, the results of the analytical and modeled copper speciation and water quality determinations were analyzed for trends and differences between sites and sample type.

The remainder of this report is organized as follows:

- Chapter 2 describes background information and a review of literature on the topics of copper speciation chemistry, copper toxicity, analytical techniques, studies on copper speciation, relevant statistical assumptions, and the chemical equilibrium models used to compare with experimental results;
- Chapter 3 discusses the sampling procedure, methods for determining the range of chemical constituents, materials and methods used for copper speciation in stormwater, evolution of the methodology, and statistical procedures used to analyze the results;
- Chapter 4 describes the copper speciation results, correlation of free ionic copper with water quality parameters, the comparison of modeled and experimental results, and the importance therein; and
- Chapter 5 is a discussion of the implications of the results of this study and recommendations for future work.

2.0 BACKGROUND

2.1 COPPER TOXICITY

Though other copper oxidation states exist, Cu^{2+} is the most stable and abundant oxidation state in aqueous environments (*USEPA 1980; 2007*). The total concentration of copper (henceforth $\text{Cu}^{2+}_{\text{tot}}$) in aqueous environments consists of the particulate, dissolved, and colloidal forms. Particulate copper is less prevalent in aquatic systems than dissolved copper (henceforth $\text{Cu}^{2+}_{\text{diss}}$) or colloidal copper, and can be a source or sink for $\text{Cu}^{2+}_{\text{diss}}$, depending on the conditions present (*Sigg and Behra 2005; USEPA 2007; Wells, et al. 1998*). In this study, $\text{Cu}^{2+}_{\text{diss}}$ is operationally defined as the fraction of copper that passes through a 0.45 μm pore size filter. In natural aquatic systems a substantial fraction of copper thus defined as dissolved is actually associated with organic colloidal particles (*Wells, et al. 1998; Sigg and Behra 2005; USEPA 2007*). Copper which is truly dissolved in natural waters is present as either a free ion (henceforth referred to as $\text{Cu}^{2+}_{\text{free}}$) or complexed with organic or inorganic ligands (compounds and elements that form coordination complexes with the metal). The toxicity of copper is directly dependent on its bioavailability to organisms; in general, bioavailability is limited to $\text{Cu}^{2+}_{\text{free}}$ and weakly complexed copper (*Brooks, et al. 2007; Luider, et al. 2004; Sigg and Behra 2005; USEPA 2007*).

In the past, both $\text{Cu}^{2+}_{\text{tot}}$ and $\text{Cu}^{2+}_{\text{diss}}$ have been utilized as primary indicators of copper toxicity. Although elevated $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{tot}}$ concentrations can suggest elevated toxicity, the complex aquatic chemistry of $\text{Cu}^{2+}_{\text{free}}$ prevents any straightforward correlations between $\text{Cu}^{2+}_{\text{tot}}$ or $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. A number of other water quality parameters affect copper toxicity: temperature, the presence of natural ligands (inorganic and organic), cation concentrations (hardness causing cations, in particular), and pH (*Luider, et al. 2004; USEPA 2007*). The effects of these parameters are summarized below in Table 2.1; a helpful diagram showing this concept is provided in Figure 2.1. Of particular importance is the presence of natural organic ligands (categorized in the table as dissolved organic carbon, DOC) that often outcompete inorganic ligands for $\text{Cu}^{2+}_{\text{free}}$ in aquatic systems and form strong complexes (*Buck and Bruland 2005*). The concentration and binding strength of organic ligands are critical factors in determining copper toxicity (*Bruland, et al. 2000; Linton, et al. 2007; Luider, et al. 2004; Plöger, et al. 2005; Sigg and Behra 2005; USEPA 2007*).

Table 2.1: Water quality parameters influencing copper toxicity

CONSTITUENT	EFFECT OF INCREASED CONSTITUENT CONCENTRATION ON COPPER TOXICITY	MECHANISM
Alkalinity (HCO_3^- , CO_3^{2-})	Decrease	Increased complexation of $\text{Cu}^{2+}_{\text{free}}$
DOC	Decrease	Increased complexation of $\text{Cu}^{2+}_{\text{free}}$
Hardness (Ca^{2+} , Mg^{2+} , Fe^{2+} , etc.)	Decrease	Competition with $\text{Cu}^{2+}_{\text{free}}$ for adsorption sites on the organism Indicator of increased inorganic ligand concentrations (<i>i.e.</i> , increased complexation of $\text{Cu}^{2+}_{\text{free}}$) Competition with $\text{Cu}^{2+}_{\text{free}}$ for DOM sites
H^+ (decreasing pH)	Increase	Competition with $\text{Cu}^{2+}_{\text{free}}$ for ligands Increased solubility ($\text{Cu}^{2+}_{\text{diss}}$)
Dissolved copper	Increase	Increased $\text{Cu}^{2+}_{\text{free}}$
Anions (NO_3^- , SO_4^{2-} , PO_4^{3-} , S^{2-} , Cl^- , etc.)	Decrease	Increased complexation of $\text{Cu}^{2+}_{\text{free}}$
Temperature	Increase	Increased solubility ($\text{Cu}^{2+}_{\text{diss}}$)

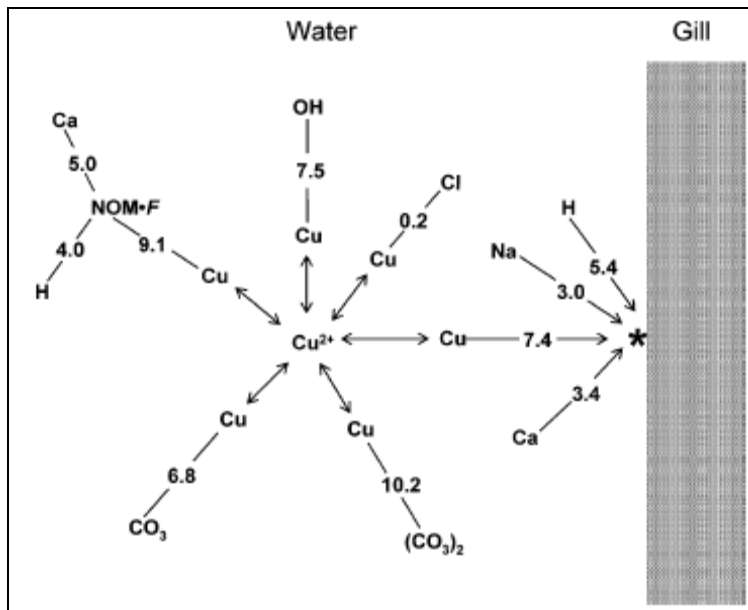


Figure 2.1: Example free ionic copper equilibrium in natural waters with modeled stability constants; taken from Luider, et al. (2004)

Importantly, none of these parameters (including $\text{Cu}^{2+}_{\text{diss}}$) can be used exclusively to determine copper toxicity; rather, toxicity is determined through direct measurement of $\text{Cu}^{2+}_{\text{free}}$ and the relative strength of copper complexes with ligands (Brooks, et al. 2007) or through the use of detailed chemical equilibrium models such as Free Ion Activity Models (FIAMs) or Biotic

Ligand Models (BLMs) (Bryan, et al. 2002; Luider, et al. 2004; USEPA 2007). Though the equilibrium models are useful, further refinement is necessary to describe the complexation of copper with natural organic matter (NOM) and various biotic ligands, and to verify modeling results using analytical data. To date, no attempts have been made to verify such models when applied to stormwater.

2.1.1 Salmonids

Most relevant to this study is the toxicity of copper in highway stormwater runoff to ESA-listed salmonid species. Recent research by Sandahl, et al. (2007) has shown that low concentrations (2-5 $\mu\text{g/L}$) of $\text{Cu}^{2+}_{\text{diss}}$ can impair the olfactory system of juvenile Coho salmon, one of several ESA-listed fish species. Damage to the chemosensory system reduces the ability of fish to navigate and avoid predators, likely increasing mortality. Much of the research on low-level copper toxicity to salmonid species has been summarized in a recent white paper by researchers at NMFS and the USGS (Hecht, et al. 2007). In short, the authors report an 8-57% reduction in predator avoidance behavior at $\text{Cu}^{2+}_{\text{diss}}$ concentrations ranging from 0.18 to 2.1 $\mu\text{g/L}$ above background ($\leq 3 \mu\text{g/L}$) levels. Furthermore, impaired olfaction resulting from short-duration (~ 10 min) exposure can last for minutes to weeks, depending on the dose.

A study by McIntyre, et al. (2008) examined the effects of water quality parameters on chemosensory deprivation in Coho Salmon. The authors found that increasing both water hardness (0.2-1.6 mM Ca) and alkalinity (0.2-3.2 mM HCO_3^-) only slightly decreased the inhibitory effects of copper. Increasing DOC (0-6 mg/L) showed a much greater capacity for protecting salmon from copper toxicity. Specifically, 19% of all surface waters collected for the study had enough DOC to reduce sub-lethal copper toxicity by half, and 2% of the sites collected in the Willamette basin had enough DOC (over 6 mg/L) to eliminate copper toxicity altogether. The relative ameliorating effects of hardness, alkalinity, and DOC were similar in a recent study examining copper's toxicity on the mechanosensory system of zebrafish (Linbo, et al. 2009). Though highway runoff is well recognized as a significant contributor to copper in natural waters, no attempts have yet been made to characterize copper speciation as a function of these water quality parameters.

2.2 CONCENTRATION AND SPECIATION IN NATURAL WATERS

The U.S. Environmental Protection Agency (EPA) has established hardness dependent water quality criteria for acute (1 hr) and chronic (96 hr) exposure to $\text{Cu}^{2+}_{\text{diss}}$. With an assumed hardness of 100 mg/L as CaCO_3 , the acute criteria is 13 $\mu\text{g/L}$, and chronic criteria is 9 $\mu\text{g/L}$ for freshwater (USEPA 2008). In marine water the acute criteria is 4.8 $\mu\text{g/L}$ and the chronic criteria is 3.1 $\mu\text{g/L}$. Currently, there are no regulations for $\text{Cu}^{2+}_{\text{free}}$ in either fresh or marine waters. Oregon freshwater and marine exposure limits are identical to federal standards.

Bowen (1985) reported typical $\text{Cu}^{2+}_{\text{diss}}$ concentrations for freshwater between 0.20-30 $\mu\text{g/L}$ and for marine water between 0.03 and 0.23 $\mu\text{g/L}$. There have been a number of studies quantifying both $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. In all cases where both parameters were reported, $\text{Cu}^{2+}_{\text{free}}$ was only a small fraction of the $\text{Cu}^{2+}_{\text{diss}}$ largely due to complexation with organic ligands. The data from these studies are presented below in Table 2.2 (for freshwater) and Table 2.3 (for marine water).

Table 2.2: Freshwater copper concentrations and speciation

STUDY	SITE	Cu ²⁺ _{diss} (µg/L) ^(a)	Cu ²⁺ _{free} (µg/L) ^(a)	DOC (mg/L)	pH
Bryan, et al. (2002)	Rivers and Lakes/Pools	NR	6.4×10 ⁻⁴ to 6.4	4.4 to 26.7	4.0 to 8.1
Plöger, et al. (2005)	High Altitude Lakes (Runoff Supplied)	0.06 to 0.1	5×10 ⁻⁸ to 2.5×10 ⁻⁷	0.3 to 2.3	5.6 to 7.6
Sigg, et al. (2006)	Swiss Lakes and Rivers	1.3 to 2.0	10 ⁻³ to 4×10 ⁻³	NR	2 ^(b)
Monticelli, et al. (2004)	Glacial Streams	0.19 to 0.45	5.1×10 ⁻⁶ to 2.0×10 ⁻⁵	NR	7.5 to 8.2
Averyt, et al. (2004)	New Zealand Alpine Lakes	0.034 to 0.54	3.2×10 ⁻¹² to 0.25	NR	5.9 to 9.0
Sigg & Behra (2005)	Hardwater Lakes and Rivers	0.32 to 2.0	6.4×10 ⁻⁹ to 2×10 ⁻⁶	NR	7.5 to 8.5
	“typical” conditions	0.64 to 6.4	6.4×10 ⁻⁷ to 6.4×10 ⁻⁵	2.8	NR
	New England Rivers	NR	6.4×10 ⁻⁴ to 6.4×10 ⁻²	NR	5.2 to 7.9
Pei, et al. (2000)	Arve River	0.13 to 0.8 ^(c)	0.08 to 0.1	NR	NR

NR – values not reported

(a) 1 µg/L of Cu is equivalent to 1.57×10⁻⁸ M

(b) samples were acidified

(c) from Cu²⁺_{tot}

Table 2.3: Marine water copper concentrations and speciation

STUDY	SITE TYPE	Cu ²⁺ _{diss} (µg/L) ^(a)	Cu ²⁺ _{free} (µg/L) ^(a)	DOC (mg/L)	pH
Hurst & Bruland (2005)	Estuarine	1.0 to 2.5	4×10 ⁻⁴ to 4×10 ⁻³	2.5 to 5.0	3.5 ^(b)
Ndungu, et al. (2005)	Estuarine	1.6 to 2 ^(c)	6.4×10 ⁻³ to 0.05	3.0 to 4.1	7.7 to 8.5
Twiss & Moffett (2002)	Coastal Marine	0.4 to 6.4	4×10 ⁻⁵ to 0.024	NR	7.5 to 8.2
Bruland, et al. (2000)	Coastal Marine	0.8	2.5×10 ⁻⁶ to 2.5×10 ⁻⁵	NR	7.9
Buck & Bruland (2005)	Coastal Marine	0.13 to 3.2	2×10 ⁻⁸ to 3.2×10 ⁻⁶	2.5 to 4.8	7.7 to 8.6
Eriksen, et al. (2001)	Coastal Marine	3.2 to 20	6.4×10 ⁻⁵ to 3.4×10 ⁻⁴	NR	2 ^(b)

NR – values not reported

(a) 1 µg/L of Cu is equivalent to 1.57×10⁻⁸ M

(b) samples were acidified

(c) from Cu²⁺_{tot}

Oregon freshwater and marine exposure limits are identical to federal standards. A collection of Oregon data collected from July 1977 to October 2006 showed Cu²⁺_{diss} concentrations ranging from <0.3 µg/L to 40.2 mg/L with a median value of <10 µg/L, and Cu²⁺_{tot} ranging from <0.05 µg/L to 570 mg/L with a median value of 12 µg/L (ODEQ 2007). According to the recent 303(d) list submitted to the EPA, eleven Oregon surface water sites are currently listed as impaired with respect to Cu²⁺_{diss} (ODEQ 2008). In a study focusing on trace elements in the Willamette River Basin, Cu²⁺_{diss} concentration ranged from <0.5 to 4.6 µg/L (14 sites sampled)

and the $\text{Cu}^{2+}_{\text{tot}}$ ranged from <0.5 to 11 $\mu\text{g/L}$ (23 sites sampled) (Anderson, et al. 1996). The USGS online water quality database (USGS 2007) reveals the presence (but not quantity) of copper at 75 of the 98 sites sampled; the quantified data reported values ranging from <1 to 20 $\mu\text{g/L}$.

2.3 COPPER IN STORMWATER

Urban stormwater runoff is an important non-point source of many contaminants present in aquatic environmental systems. In 1983, the EPA's National Urban Runoff Program (NURP) examined the effects of urban stormwater runoff on receiving water quality (Athayde, et al. 1983). Among the main conclusions of this project was that heavy metals are the most prevalent priority pollutant found in urban stormwater, and that the effect stormwater runoff had on receiving waters was highly site-specific. The results of the NURP showed that copper was prevalent in highway stormwater runoff and that it was a potential source of toxicity to aquatic organisms (Athayde, et al. 1983). Specifically, copper was detected in 91% of the NURP samples and had a median Event Mean Concentration (EMC) of 34 $\mu\text{g/L}$ (Athayde, et al. 1983). The end-of-pipe total copper concentrations exceeded the EPA's acute freshwater criteria (~10-40 $\mu\text{g/L}$, depending on the hardness of the water) 47% of the time. This value is comparable to the 36-43% of sites that exceeded the ambient standards in a more recent study performed by the Oregon Association of Clean Water Agencies (Strecker, et al. 1997). In another study, copper and zinc caused 90% of the toxicity in assays in which various aquatic species were exposed directly to roadway stormwater runoff (Kayhanian, et al. 2007). These results show that copper is not only commonly found in highway runoff, but that it also often exceeds existing standards for acute toxicity in aquatic species. However, most existing standards are conservative estimates based on $\text{Cu}^{2+}_{\text{tot}}$ loadings, and do not account for the speciation of copper in the runoff.

2.3.1 Primary Sources

The primary source of copper in highway stormwater runoff is brake pad wear. Brake pads can contain anywhere from 0-20% copper by mass (Rosselot 2006a). A 2006 study in the San Francisco Bay area estimated that brake pad linings released approximately 0.58 mg copper per vehicle per km driven (Rosselot 2006a). Another study found brake linings to be the dominant source of copper in highway runoff (Legret and Pagotto 1999). Brake pad wear also contributes significantly to atmospheric copper concentrations (Rosselot 2006a). Atmospheric deposition is an especially important source of copper in runoff from urban areas (Sabin, et al. 2005). Dry deposition has been found to be the dominant mechanism in dry climates, while wet deposition becomes increasingly important in wet climates (Sabin, et al. 2005). Wu and coworkers (1998) found deposition to contribute 30-50% of the copper in highway runoff loadings. Other sources of copper to stormwater runoff include: engine oil, combustion of lubricating oils, roof/gutter runoff, building siding corrosion, fertilizer, pesticides, industrial releases, and wet and dry deposition (Davis, et al. 2001; Kim and Fergusson 1994; Makepeace, et al. 1995; Rosselot 2006b).

2.3.2 Concentration, Partitioning, and Speciation in Stormwater

Typical total copper concentrations in stormwater range from below the detection limit (often 1 µg/L) to several hundred µg/L, with medians in the 10-40 µg/L range. Dissolved copper concentrations measured below detection limits more often than $\text{Cu}^{2+}_{\text{tot}}$ (Bannerman, et al. 1996; Strecker, et al. 1997); concentrations ranged from below the detection limit to ~100 µg/L, with median values of 3-12 µg/L (Bannerman, et al. 1996; Driscoll, et al. 1990; Harrison, et al. 1997; Kayhanian, et al. 2003; Strecker, et al. 1997; USEPA 1983; WERF, et al. 2007). The Kayhanian, et al. (2003) study focused specifically on runoff generated from highways and showed a median for $\text{Cu}^{2+}_{\text{tot}}$ of 20.2 µg/L (ranging from 1-9500 µg/L) and a median for $\text{Cu}^{2+}_{\text{diss}}$ of 9.9 µg/L (ranging from 1-121 µg/L). Table 2.4 and Table 2.5 below show the copper concentrations from some significant stormwater studies.

Table 2.4: Total copper in stormwater from previous studies

STUDY	LOCATION	NUMBER OF SITES	RANGE OF $\text{Cu}^{2+}_{\text{tot}}$ (µg/L)	MEDIAN $\text{Cu}^{2+}_{\text{tot}}$ (µg/L)
Kayhanian, et al. (2003)	California	83	1-9500	20.2
Bannerman, et al. (1996)	Wisconsin	14	<3-210	18
USEPA (1983)	Nationwide	51	4-349 ^(a)	34
Driscoll, et al. (1990)	Nationwide	22	9-120 ^(b)	39
WERF, et al. (2007)	Nationwide	122	1.3-874.5 ^(c)	20.1 ^(c)
Harrison, et al. (1997) ^(d)	Oregon	8	1-45	8
Strecker, et al. (1997)	Oregon	51	<1-250	11.5

- (a) Based on 90% confidence intervals at specific sites
- (b) Based on 90% data values from urban and non-urban sites
- (c) Based on high/low/median mean site values from the 122 sites studied
- (d) Urban surface water sites heavily influenced by stormwater

Table 2.5: Dissolved copper in stormwater from previous studies

STUDY	RANGE OF $\text{Cu}^{2+}_{\text{dis}}$ (µg/L)	MEDIAN $\text{Cu}^{2+}_{\text{dis}}$ (µg/L)	MEDIAN % DISSOLVED ^(a)
Kayhanian, et al. (2003)	1-121	9.9	49.1%
Bannerman, et al. (1996)	<3-33	5	27.8%
WERF, et al. (2007)	1.5-45.5 ^(b)	11.6 ^(b)	57.8%
Harrison, et al. (1997) ^(c)	1-21	3.5	43.8%
Strecker, et al. (1997)	<1-110	4	34.8%

- (a) Based on quotient of dissolved median Cu to total median Cu, for each study
- (b) Based on high/low/median mean site values from the 122 sites studied
- (c) Urban surface water sites heavily influenced by stormwater

As shown above, copper is typically found in both the particulate and dissolved fractions of stormwater runoff (Dean, et al. 2005; Grant, et al. 2003; Prestes, et al. 2006). The dissolved

fraction is most commonly between 30 and 70% of the total copper in runoff, as indicated in Table 2.5 and by Breault and Granato (2000). However, the dissolved fraction can approach 100% during snowmelt events (Breault and Granato 2000). The dissolved fraction is of immediate concern to aquatic species, though the particulate-bound fraction can be released into the environment as well. Tuccillo (2006) found that copper in runoff was predominantly attached to particles $> 5 \mu\text{m}$ or in the dissolved phase (here defined as passing through a 10 kDa filter).

Few studies have examined the speciation of dissolved copper in stormwater. Dean and coworkers (2005) examined the aqueous phase metal speciation using a chemical equilibrium model (MINTEQ) and found that copper speciation varied with storm event hydrology and, in some cases, varied over the course of individual storms. Generally, Cu-DOM (dissolved organic matter) and CuCO_3 species were found to be the most prevalent, but $\text{Cu}^{2+}_{\text{free}}$ was a significant species in their models (about 8-40%). Factors affecting the speciation included: rainfall intensity, rainfall pH, concentration of copper, concentration of ligands, and alkalinity.

2.4 FACTORS AFFECTING COPPER IN RUNOFF

2.4.1 First Flush

Heavy metals, total suspended solids (TSS), and other stormwater pollutants often exhibit a “first flush” effect at the beginning of a storm. Though it has been defined in different ways, the first flush effect can be most generally defined as more mass of a pollutant being washed off during the beginning of a storm than is washed off during the end – i.e., the first portion of a storm flushes most of the pollutants that were collected on the road surface prior to the storm. Mathematically, this effect can be described as follows:

$$\frac{m(t)/M}{v(t)/V} \geq 1$$

where $m(t)$ and $v(t)$ represent the cumulative mass of pollutant and the cumulative runoff volume washed off at any given time, t , respectively, while M and V represent the total mass of pollutant and total runoff volume for the entire storm, respectively.

As this ratio increases, it indicates an increasingly pronounced first flush. Noting a first flush can be helpful in determining what best management practices (BMPs) may be useful in controlling stormwater runoff (Sansalone and Cristina 2004). Using the above criteria, Flint and Davis (2007) found that a first flush of $\text{Cu}^{2+}_{\text{tot}}$ occurred in 79% of the storms studied.

The first flush effect lends itself to certain types of storms more than others. Storms of short duration and relatively constant rainfall intensity (mass-limited) have exhibited the first flush effect more than other storms (Barrett, et al. 1998). These mass-limited hydrologic events result in pollutant delivery that is disproportionately higher towards the beginning of the event (Dean, et al. 2005; Deletic and Maksimovic 1998; Sansalone and Buchberger 1997). Low intensity hydrologic events are considered “flow-limited” and result in pollutant delivery that is roughly

proportional to the storm hydrograph (Dean, et al. 2005; Sansalone and Buchberger 1997). As such, flow-limited events often do not exhibit first flush behavior. Sansalone and Buchberger (1997) showed a first flush for $\text{Cu}^{2+}_{\text{diss}}$ in flow-limited and mass-limited events; evidence of a first flush for particulate-bound species was not so well-defined.

The first flush effect has also been witnessed with respect to toxicity. In a study involving various aquatic species and pollutants, over 40% of the toxicity typically stemmed from the first 20% of discharged runoff volume (Kayhanian, et al. 2007). This study also showed that toxic effects were rarely observed in organisms exposed to composite samples, even when a storm exhibited strong first flush behavior.

Snowmelt runoff events can also affect the amount of copper in runoff. Snowmelt events are typically less intense than rainfall events, but extend for longer durations. However, due to the ground being either frozen or saturated, more runoff results from snowmelt events than would be expected for a similar rain event (Driscoll, et al. 1990). Total median metal concentrations have been shown to increase by a factor of ~2.5 for snowmelt events (as compared to rainfall events) (Driscoll, et al. 1990). However, the receiving water impacts of snowfall events may be mitigated by the effects of dilution due to the large volume of runoff.

2.4.2 Hydrologic Effects

Total event rainfall and runoff volume have been hypothesized to correlate to the event mean concentration (EMC) of a contaminant, either by causing increased wash-off of pollutants or by increased dilution. The EMC is the measurement most often used to describe the amount of a pollutant washed off during a given storm. The EMC is defined as the flow-weighted average concentration of the pollutant over the course of one full hydrologic event. Mathematically, it can be defined as follows:

$$EMC = \frac{\int_0^T C(t)Q(t)dt}{\int_0^T Q(t)dt}$$

where $C(t)$ is the concentration of the pollutant at time t , $Q(t)$ is the flow rate at time t , and T is the duration of the entire runoff event.

This equation can be similarly represented in summation form for discrete data points. Although these values are useful, EMCs give no information on how the concentration of a pollutant varies with respect to time – i.e., the concentration of a pollutant at a given point in time during the event may be higher or lower than the EMC for the entire event.

Reports studying the relationship between total rainfall and pollutant EMCs typically found weak negative correlations, indicating the effect of dilution may be dominant (Driscoll, et al. 1990; Kayhanian, et al. 2003; USEPA 1983). Similarly, Kayhanian, et al. (2003) found increasingly intense rainfall did not correlate significantly with $\text{Cu}^{2+}_{\text{tot}}$ and correlated negatively with $\text{Cu}^{2+}_{\text{diss}}$ EMCs. This result indicates that rainfall intensity is closely tied to total event rainfall – meaning

that the effects of dilution were more important than any increased wash-off effect caused by more intense rainfall. However, as noted earlier, increasingly intense storms often have a more pronounced first flush. These results suggest that although the EMC from an intense storm may be lower than that of a calmer storm, the copper concentration early in the intense storm may be higher than it would be at any point during a calmer storm.

2.4.3 Traffic Effects

The average daily traffic (ADT) has been shown to influence the amount of copper found in runoff. However, this effect is generally very broad and a poor predictor of pollutant concentrations. In one study, urban highways (classified as ADT > 30,000 vehicles/day) had a median of 54 $\mu\text{g/L}$ $\text{Cu}^{2+}_{\text{tot}}$ while non-urban highways showed a median of 22 $\mu\text{g/L}$ in stormwater runoff (*Driscoll, et al. 1990*). There was little correlation found between copper concentrations and ADT beyond sites that are considered urban or non-urban. This finding was echoed in a study by Kayhanian, et al. (2003) where they found a significant difference between sites that are considered urban (same ADT criteria as above) and non-urban, but there was no significant difference distinguishing between sites with ADTs ranging from 30,000 to over 200,000 vehicles/day. Urban highways, when compared to each other at different ADT volumes, often do not exhibit a significant difference in $\text{Cu}^{2+}_{\text{tot}}$ EMC. Other traffic-related variables, such as traffic during storms and braking intensity, have rarely been studied, but may also alter copper concentration in highway runoff.

2.4.4 Other Effects

Antecedent Dry Period (ADP), the period of time between the end of one storm and the start of the next one, has been correlated to pollutant EMCs in previous studies. Longer ADPs would be expected to allow more pollutants to build up on the roadway prior to being washed off by the next storm. Previous studies in California and Nevada reported that dissolved pollutant loads on streets may reach a steady-state value within approximately 1-2 weeks, after which the mass of pollutants deposited onto the surface does not increase (*Soller, et al. 2005*). Therefore, ADPs significantly longer than 2 weeks may not yield significantly different dissolved pollutant loads than storms with 1-2 week ADPs. Some studies have shown longer ADPs to have a significant positive correlation with higher EMCs (*Kayhanian, et al. 2003; Prestes, et al. 2006*). However, other studies have shown that the influence of ADP on pollutant EMCs may be substantially diminished by other transportation processes (natural and vehicular-induced wind, material pick-up by tires) that influence pollutant build-up during the dry period (*Irish, et al. 1995*).

Primary land use in areas surrounding highways has also been thought to affect pollutant concentrations. The NURP did not find any statistically significant variations in EMCs between land use categories, outside of the differences between urban and non-urban categories (*Athayde, et al. 1983*). The report concluded that if land use category does have an effect, it seems to be eclipsed by storm-to-storm variability. Kayhanian, et al. (2003) determined that land use category (with the exception of industrial and mixed-use) did not have a significant correlation to $\text{Cu}^{2+}_{\text{tot}}$ EMCs, especially when other variables (event rainfall, ADP, cumulative precipitation, and ADT) were taken into account; higher than average copper concentrations were found in industrial and mixed land use areas.

The NURP also did not find any consistent relationship between copper EMCs and location (*Athayde, et al. 1983*). Additionally, significant differences in copper concentrations found in geographically distinct locations are likely due to other parameters (*e.g.*, ADP, urban/non-urban location, rainfall characteristics).

2.5 COPPER SPECIATION THEORY

As mentioned above, copper can exist in three different “compartments” in aqueous environments: particulate, colloidal, and dissolved. This can be summarized simply as:

$$[Cu_{tot}^{2+}] = [Cu_{part}^{2+}] + [Cu_{col}^{2+}] + [Cu_{diss}^{2+}] \quad (2-1)$$

where $[Cu_{tot}^{2+}]$ refers to the total concentration of copper within the system consisting of particulate $[Cu_{part}^{2+}]$, colloidal $[Cu_{col}^{2+}]$, and dissolved $[Cu_{diss}^{2+}]$ copper.

Within each environmental compartment, copper can exist in many different forms or “species.” Cu_{diss}^{2+} presents the most acute threat to aquatic species due to its bioavailability, although some dissolved species are more bioavailable/toxic than others. Therefore, the accurate determination of the speciation of copper in the dissolved form is essential for assessing the potential toxicity of a given water.

In the aqueous environment, Cu_{free}^{2+} forms complexes with many inorganic and organic ligands. When present, copper preferentially binds to organic ligands (*Buck and Bruland 2005*). The total concentration of Cu_{diss}^{2+} in the natural environment can be described by the following mass balance equation (*Campos and van den Berg 1994*):

$$[Cu_{diss}^{2+}] = [Cu_{free}^{2+}] + \sum_i (\beta'_{CuL} [L'_i] [Cu_{free}^{2+}]) + \sum_i (\beta'_{CuX_n} [X'_i]^n [Cu_{free}^{2+}]) + \sum \left(\beta'_{CuOH_n} \frac{[Cu_{free}^{2+}]}{[H^+]^n} \right) \quad (2-2)$$

where $[Cu_{diss}^{2+}]$ is the total dissolved copper concentration including free ionic copper ($[Cu_{free}^{2+}]$) and copper bound with organics, $[L'_i]$ and inorganics, $[X'_i]$. β'_{CuL} and β'_{CuX} represent the conditional stability constants for each of the organic and inorganic copper-ligand complexes, respectively. β'_{CuOH} is the acidity constant for stormwater. n is the stoichiometric coefficient for the given ion.

2.5.1 Analytical Techniques for Quantifying Free Ionic Copper

Analytical techniques typically used to quantify copper in water (such as Inductively Coupled Plasma Mass Spectrometry) are not capable of measuring Cu_{free}^{2+} without a separation step. With the rising concern of copper toxicity in natural aquatic environments, a number of analytical techniques have been developed for measurement of metal speciation in natural environments. These techniques and instruments include:

- Diffusive Gradient in Thin Films (DGT)
- Donnan Membrane Technique (DMT)
- Permeation Liquid Membranes (PLM)
- Ion Selective Electrodes (ISE)
- Anodic Stripping Voltammetry (ASV)
- Gel Integrated Microelectrodes (GIME)
- Stripping Chronopotentiometry (SCP)
- Competitive Ligand Exchange/Adsorptive Cathodic Stripping Voltammetry (CLE-ACSV)

Each technique can be characterized as either a dynamic- or equilibrium-based technique, although some techniques can be employed in either mode. Dynamic techniques recognize and account for the kinetics of copper binding reactions. As such, these techniques are characterized by measuring labile Cu^{2+} rather than $\text{Cu}^{2+}_{\text{free}}$. A complex is considered labile if it is prone to change, or likely to undergo one. Lability is an operationally defined characteristic that depends on the technique's response and accumulation time (*Sigg, et al. 2006*). In general, labile Cu^{2+} includes $\text{Cu}^{2+}_{\text{free}}$ and Cu^{2+} weakly complexed with organics and inorganics.

Equilibrium techniques typically determine $\text{Cu}^{2+}_{\text{free}}$ after allowing the solution to equilibrate with, or without, an added ligand. Equilibrium techniques are commonly used to determine chemical species distribution and are essential to understanding the fate of constituents in aqueous systems; however, it is important to note the possible kinetic dependence of the reactions (*Scally, et al. 2003*). Table 2.6 and Table 2.7 below summarize the important characteristics and advantages and disadvantages for each of these techniques.

Table 2.6: Summary of analytical techniques for quantifying free ionic copper

TECHNIQUE	MODE	IN SITU	DETECTION LIMIT ($\mu\text{g/L}$) ^(a)	
			FRESHWATER	MARINE WATER
DGT	Dynamic	Yes	8.3×10^{-2}	$5.8 \times 10^{-2(b)}$
DMT	Dynamic or Equilibrium	Yes	$7.3 \times 10^{-4(b)}$	Not Available
PLM	Dynamic or Equilibrium	Yes	$6.4 \times 10^{-5(b)}$	$5.7 \times 10^{-2(c)}$
ISE	Equilibrium	Yes	$6.4 \times 10^{-3(d)}$	$6.4 \times 10^{-3(d)}$
ASV	Dynamic	Yes	5×10^{-3}	5×10^{-3}
GIME	Dynamic	Yes	6.4×10^{-3}	1.3×10^{-2}
SCP	Dynamic	No	$2.5 \times 10^{-3(c)}$	0.7
CLE-ACSV	Equilibrium	No	$2.9 \times 10^{-8(c)}$	$< 1.3 \times 10^{-6(e)}$

Notes:

- 1 $\mu\text{g/L}$ of Cu is equivalent to 1.57×10^{-8} M
- long preconcentration times (*Parthasarathy, et al. 2001*)
- lowest reported value (detection limit not reported)
- using metal ion buffers
- calculated based on the reported detection limit of $\text{Cu}(\text{SA})_x$ of 0.1 nM and the competition strength of the binding ligand (*Campos and van den Berg 1994*).

Table 2.7: Advantages and disadvantages for copper speciation analytical techniques

TECHNIQUE	ADVANTAGES	DISADVANTAGES
DGT ^(a)	<ul style="list-style-type: none"> No power supply required Determines disassociation rate of weak copper complexes 	<ul style="list-style-type: none"> Long accumulation time (days) to measure low metal concentrations Measures labile Cu²⁺, not Cu²⁺_{free}
DMT ^(b)	<ul style="list-style-type: none"> Simultaneous metal determination 	<ul style="list-style-type: none"> Requires long equilibration times (1-4 days) in equilibrium mode to measure low metal concentrations HCO₃⁻, CO₃²⁻, and OH⁻ can complex with Cu²⁺_{free} and cause measurement errors
PLM ^(c)	<ul style="list-style-type: none"> Provides time-averaged copper concentrations 	<ul style="list-style-type: none"> Long accumulations time (hours) required Only used in one previous study on copper speciation
ISE ^(d)	<ul style="list-style-type: none"> Simple operation Measures <i>activity</i> of Cu²⁺_{free} as opposed to molar concentration 	<ul style="list-style-type: none"> Membrane fouling by organics Cross contamination Slow response time at low ion concentrations Declining performance over the lifespan of the electrode
ASV ^(e)	<ul style="list-style-type: none"> Simultaneous metal determination Can be combined with competitive ligand techniques to characterize copper-organic complex strengths 	<ul style="list-style-type: none"> Electrode fouling by organics Measures labile Cu²⁺, not Cu²⁺_{free}
GIME ^(f)	<ul style="list-style-type: none"> Simultaneous metal determination Gel layer prevents electrode fouling and provides qualitative information relative concentrations of mobile and colloidal copper-ligand complexes 	<ul style="list-style-type: none"> Use in traditional metal titrations shows artifacts at high copper concentrations Measures labile Cu²⁺, not Cu²⁺_{free}
SCP ^(g)	<ul style="list-style-type: none"> Oxidation step allows for determination of metal:ligand ratio Used in media with high organic content 	<ul style="list-style-type: none"> Must account for oxygen concentration in sample
CLE-ACSV ^(h)	<ul style="list-style-type: none"> Used in many previous speciation studies Highly sensitive Determines binding strength of copper with natural ligands in the sample 	<ul style="list-style-type: none"> Metal titrations are time-consuming Sensitive to surfactants in natural waters Oversaturation of Cu-ligand complexes at the mercury drop is possible

References:

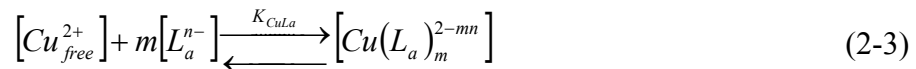
- (a) (Meylan, et al. 2004; Scally, et al. 2003; Sigg, et al. 2006; Twiss and Moffett 2002)
(b) (Kalis, et al. 2007; Sigg, et al. 2006; Temminghoff, et al. 2000; Weng, et al. 2001; Weng, et al. 2005)
(c) (Ndungu, et al. 2005; Sigg, et al. 2006; Zhang, et al. 2007)
(d) (De Marco, et al. 2007; Eriksen, et al. 2001)
(e) (Bruland, et al. 2000; Buck and Bruland 2005; Howell, et al. 2003; Hurst and Bruland 2005)
(f) (Pei, et al. 2001; Pei, et al. 2000; Sigg, et al. 2006)
(g) (Pei, et al. 2001; Pei, et al. 2000; Serrano, et al. 2007; Sigg, et al. 2006; Town 1998)
(h) (Bruland, et al. 2000; Eriksen, et al. 2001; Miller and Bruland 1997; Rue and Bruland 1995; Sigg, et al. 2006; Twiss and Moffett 2002)

In general, equilibrium techniques have lower detection limits than dynamic techniques. Furthermore, many techniques require long equilibration or preconcentration/accumulation times to achieve the values stated in the table (e.g., DGT, DMT, PLM, GIME and ISE). CLE-ACSV is the most sensitive analytical method, with detection limits more than an order of magnitude lower than the closest competitor. Detection limits reported in Table 2.6 are conservative estimates based on low concentrations of the competing ligand and a deposition time of 1 min. CLE-ACSV outperformed several other techniques (DGT, ISE, GIME, PLM, SCP, and DMT) in terms of detection limits for free metal concentrations (Sigg, *et al.* 2006; Xue and Sunda 1997). Another major advantage of CLE-ACSV is that it can be used to determine the relative strength of the naturally occurring Cu-ligand complexes. Because copper speciation in stormwater has not been analytically examined, this added capability is quite valuable. Determination of binding strengths between copper and organic matter present in stormwater will aid in verifying results generated using equilibrium models. These advantages made CLE-ACSV an attractive choice for the current study.

The primary disadvantage of CLE-ACSV is its inability to be used *in situ*. The advantages of dynamic *in situ* techniques are the lack of sample preparation and the ability to account for the kinetic aspects of copper complexation. That being said, the techniques that can be used *in situ* often require deployment/accumulation or equilibration times that are longer than typical storm event durations. Because copper speciation has been shown to vary over the course of an individual storm and copper olfactory toxicity to juvenile salmonids can occur over short exposure times, use of these *in situ* techniques will not yield the temporal resolution necessary to experimentally verify these effects. Furthermore, many of the alternative techniques have high detection limits (relative to CLE-ACSV), are prone to electrode fouling by colloids and NOM, and are unable to measure $\text{Cu}^{2+}_{\text{free}}$ alone. On these merits, it was determined that CLE-ACSV was the most appropriate technique for use in this study.

2.5.1.1 CLE-ACSV

CLE-ACSV has been used to quantify both free metal ion concentrations and the relative binding strengths of several transition metals with natural ligands (Rue and Bruland 1995; Miller and Bruland 1997; Buck and Bruland 2005; Sigg, Black, *et al.* 2006). CLE-ACSV consists of three primary steps. First, a competing ligand, L_a , is added to a natural water sample and allowed to equilibrate; during equilibration, some of the dissolved Cu^{2+} complexes with the added ligand (see Equation (2-3)). The variables m and n are the stoichiometric coefficients and molecular charge, respectively.



Second, the CuL_a complex is adsorbed onto a hanging mercury drop electrode; it is this pre-concentration step that results in extremely low detection limits (Wang 1985). Finally, Cu^{2+} is reduced to Cu^0 by cathodically scanning the potential (towards more negative values). The induced current is proportional to the amount of Cu^{2+} adsorbed onto the mercury drop. By titrating the original sample (and the added competitive ligand) with copper, the $\text{Cu}^{2+}_{\text{free}}$ concentration and the relative binding strengths of

copper with the naturally present ligands can be determined. Selection of the added ligand depends on the metal ion of interest, the electroactivity of the metal-ligand complex, and the ability of the complex to adsorb to mercury (*Rue and Bruland 1995*).

The primary compound adsorbed by the mercury drop is in the form $Cu(L_a)_m^0$. The instrument response can be modeled as the following equation:

$$i_p = S[Cu(L_a)_m] \quad (2-4)$$

where i_p is the current measured by the instrument and S is a proportionality constant (sensitivity) of the method.

2.5.2 Determining Copper Speciation

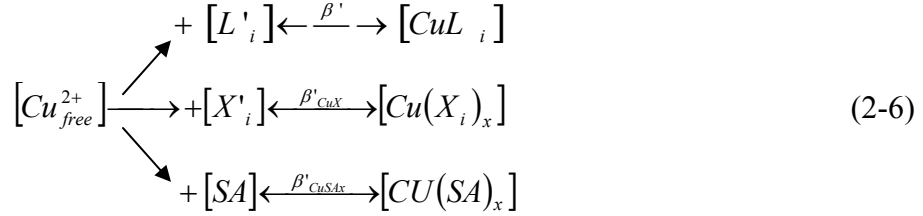
In order to determine the speciation of copper in an aquatic system, Equation (2-4) needs to be solved. Techniques such as inductively coupled plasma spectroscopy can be used to determine the Cu^{2+}_{diss} concentration; ion chromatography and alkalinity titrations can measure inorganic ligand concentrations; and many stability constants are tabulated in literature (*Martell and Smith 1995*). The remaining unknowns are the concentration and binding strength of the organic ligands. These are determined with CLE-ACSV. Once determined, Equation (2-2) can be solved for the Cu^{2+}_{free} concentration.

As described above, CLE-ACSV requires the addition of an added ligand that binds with copper to form an electroactive complex. There are multiple ligands that have been used for copper speciation, including: catechol (*van den Berg 1984*), tropolone (*Donat and van den Berg 1992*), ethylenediamine (*Scarano, et al. 1990*), 8-hydroxyquinoline (*van den Berg 1986*), and salicylaldehyde (*Buck and Bruland 2005; Campos and van den Berg 1994; Kogut and Voelker 2001; Monticelli, et al. 2004; Plöger, et al. 2005*). Of these ligands, salicylaldehyde (SA) is the most sensitive (to copper) and thus leads to greater signal responses; SA also allows a larger detection range of complex strengths (β'_{CuL}) (*Campos and van den Berg 1994*). For these reasons, SA was selected as the added ligand in the present work.

In the presence of SA, Equation (2-2) becomes:

$$[Cu]_{diss} = [Cu^{2+}] + \sum_i (\beta'_{CuL} [L_i] [Cu^{2+}]) + \sum_i (\beta'_{CuX_n} [X_i]^n [Cu^{2+}]) + \sum (\beta'_{CuOH_n} [Cu^{2+}] / [H^+]^n) + \alpha_{CuSAx} [Cu^{2+}] \quad (2-5)$$

This competition between SA, inorganic ligands, X_i , and organic ligands, L_i , can be described in an equilibrium equation also:



As shown in Equation (2-5), condition-specific alpha values for the complex CuSA, α_{CuSAx} , are essential components in determining the speciation of copper. α_{CuSAx} , as defined by Campos and van den Berg (1994), is:

$$\alpha_{CuSAx} = K'_{CuSA} [SA'] + \beta'_{CuSA2} [SA']^2 \quad (2-7)$$

Where $[SA']$ is the concentration of unbound SA in solution and K'_{CuSA} and β'_{CuSA2} are conditional stability constants for the complex $CuSA^+$ and $Cu(SA)_2$, respectively. In actuality CLE-ACSV is thought to measure the complex $Cu(HSA)_2$, but this compound is commonly referred to in literature as simply $Cu(SA)_2$. Henceforth these terms will be considered interchangeable.

2.5.3 Previous Work with Salicylaldoxime

Salicylaldoxime has been used for copper speciation studies in rain water, seawater, and fresh water (Buck and Bruland 2005; Campos and van den Berg 1994; Kogut and Voelker 2001; Monticelli, et al. 2004; Plöger, et al. 2005; Witt and Jickells 2005). Campos and van den Berg (1994) first proposed use of SA in copper speciation due to its greater sensitivity to copper (3-4 fold greater) compared with previous added ligands (tropolone, 8-quinolinol, and catechol) and its detection window that is centered in between the detection limits of tropolone and 8-quinolinol.

Alpha values for CuSA were calculated in sea water conditions with varying salinity (representing estuaries) and in glacier water with varying calcium concentrations. Table 2.8 shows a list of determined α_{CuSAx} values. Table 2.9 and Table 2.10 include a list of copper speciation results obtained with SA; all but Monticelli and coworkers use alpha values determined by Campos and van den Berg. Ligand concentrations and binding strengths are represented by $[L_x]$ and K_{CuLx} respectively, where x is a demarcation for weak and strong ligand classes in the Buck and Bruland study. Cu^{2+}_{diss} concentrations range from 3.1 to 49.6 nM for seawater studies; 2.9 to 6.3 nM for glacier supplied streams; and 1.4 to 80.1 nM in rainwater studies. Cu^{2+}_{free} concentrations were generally low, the highest ($10^{-12.2}$ M) was from a continental rainstorm and the lowest ($10^{-15.5}$ M) was from the Grizzly Bay, San Francisco (Bay).

Table 2.8: Literature alpha values for Cu-SA complex

SA CONCENTRATION (μM)	$\log \alpha_{\text{CuSAx}}$	STANDARD DEVIATION	CONDITIONS
2	4.71 ^a	0.03	Seawater with Salinity of 1 psu, pH 8.35
10	5.87 ^a	0.09	
25	6.60 ^a	0.07	
2	3.85 ^a	0.20	Seawater with Salinity of 35 psu, pH 8.35
25	5.83 ^a	0.20	
2	3.94 ^b	0.02	0.4 ppm Calcium, pH 7.68
10	4.81 ^b	0.01	
25	5.19 ^b	0.01	
25	5.16 ^b	0.01	0.4 ppm Ca, pH 7.68
25	5.16 ^b	0.01	4 ppm Ca, pH 7.68
25	4.75 ^b	0.01	20 ppm Ca, pH 7.68

References:

a) (*Campos and van den Berg 1994*)b) (*Monticelli, et al. 2004*)**Table 2.9: A list of copper speciation data determined in seawater in previous studies through CLE-ACSV and SA**

SITE	$[\text{Cu}^{2+}_{\text{diss}}]$ (nM)	$\text{Log} [\text{Cu}^{2+}_{\text{free}}]$ (M)	$\text{Log } K_{\text{CuL1}}$ (K_{CuL2})	$[\text{L}_1]$ ($[\text{L}_2]$) (nM)	CONDITIONS
Dumbarton Bridge (Jan 03) ^a	33.7	-14.0	13.9 (12.1)	48 (135)	Salinity: 21.7 psu
Dumbarton Bridge (Mar 03) ^a	27.0	-14.0	14.3 (12.6)	29 (78)	Salinity: 22.8 psu
Redwood Creek (Jan 3) ^a	26.4	-13.5	13.4 (12.7)	25 (75)	Salinity: 22.9 psu
Redwood Creek (Mar 03) ^a	25.0	-13.6	13.9 (12.9)	27 (66)	Salinity: 23.6 psu
San Bruno Shoals (Jan 03) ^a	22.9	-13.5	13.1 (12.2)	42 (85)	Salinity: 22.9 psu
San Bruno Shoals (Mar 03) ^a	27.1	-13.3	13.8 (12.3)	31 (64)	Salinity: 25.6 psu
Yerba Buena Island (Jan 03) ^a	18.9	-13.5	12.9 (12.1)	58 (75)	Salinity: 21.1 psu
Yerba Buena Island (Mar 03) ^a	17.9	-13.3	14.0 (12)	22 (48)	Salinity: 26.4 psu
San Pablo Bay (Jan 03) ^a	25.0	-14.5	14.0 (12.4)	68 (78)	Salinity: 13.0 psu
San Pablo Bay (Mar 03) ^a	20.3	-13.8	13.6 (12.6)	45 (55)	Salinity: 17.3 psu
Grizzly Bay (Jan 03) ^a	27.7	-15.5	13.5	265	Salinity: 0.0 psu
Grizzly Bay (Mar 03) ^a	49.6	-15.5	14.0 (12.8)	247 (133)	Salinity: 0.5 psu
Mediterranean ^b	3.1	nr	13.3	10.8	Tested at 2 μM SA
Atlantic ^b	1.55	nr	13.1	4.9	Tested at 2 μM SA

References:

nr: value not reported

a) (*Buck and Bruland 2005*), all samples are seawater at pH 8.2b) (*Campos and van den Berg 1994*), all samples are seawater at pH 8.35

Table 2.10: A list of copper speciation data determined in freshwater in previous studies through CLE-ACSV and SA

SITE	[Cu ²⁺ _{diss}] (nM)	Log [Cu ²⁺ _{free}] (M)	Log K _{CuL1} (K _{CuL2})	[L ₁] ([L ₂]) (nM)	CONDITIONS
Rutor 1 ^a	4.3	nr	12.5	10.2	Distance from source: 0 km
Rutor 2 ^a	6.3	nr	12.9	9.1	0.50 km
Rutor 3 ^a	6.9	nr	12.7	11.6	0.96 km
Rutor 4 ^a	5.2	nr	12.4	16.0	1.64 km
Rutor 5 ^a	5.6	nr	12.9	11.9	2.56 km
Rutor 6 ^a	2.9	nr	12.5	9.6	4.04 km
Rutor 7 ^a	4.8	nr	12.5	13.4	7.67 km
Rutor 8 ^a	3.6	nr	12.5	15.7	10.06 km
Rutor 9 ^a	3.1	nr	12.7	10.6	14.03 km
Redo (Nov 00) ^b	1.4	-15.1	14.0	20.2	Altitude: 2,235m
Redo (May 01) ^b	1.4	-14.8	13.9	13.3	
Redo (Sep 01) ^b	1.7	-14.8	13.8	20.8	
Ladove Pleso (Sep 00) ^b	1.2	-15.0	13.8	18.5	Altitude: 2,057m
Ladove Pleso (Jul 01) ^b	1.0	-14.4	13.5	12.2	
Event #446 ^c	11.1	nr	15.5	10.5	Mixed storm
Event #478 ^c	22.0	-13.8	14.0	35.2	Mixed storm
Event #488 ^c	80.1	-12.2	13.8	82.2	Continental storm
Event #493 ^c	23.5	-14.1	14.5	32.4	Continental storm
Event #494 ^c	10.3	nr	nr	nr	Marine storm
Event #496 ^c	23.6	-15.3	15.8	31.1	Marine storm
Event #534 ^c	78.5	nr	14.0	64.5	Mixed storm
Event #540 ^c	11.4	-13.2	14.0	13.1	Mixed storm
Event #553 ^c	10.2	nr	14.0	6.5	Marine storm
Event #554 ^c	55.1	nr	13.9	30.4	Mixed storm
Event #559 ^c	2.1	-15.2	14.7	8.3	Continental storm
Event #562 ^c	49.8	nr	14.0	12.5	Mixed storm
Event #563 ^c	21.0	-14.5	15.5	23.1	Mixed storm
Event #564 ^c	26.0	-13.3	13.9	32.9	Mixed storm
Event #567 ^c	37.8	nr	14.7	34.6	Mixed storm
Event #568 ^c	23.0	nr	nr	nr	Mixed storm
Event #570 ^c	1.4	-15.1	15.1	2.9	Mixed storm
Event #572 ^c	12.9	nr	15.0	9.2	Mixed storm
Event #575 ^c	7.0	nr	nr	nr	Continental storm
Event #577 ^c	10.0	nr	16.1	6.2	Mixed storm
Event #578 ^c	4.4	nr	14.5	3.8	Marine storm
Event #580 ^c	3.4	-14.7	14.2	13.3	Mixed storm
Event #582 ^c	2.5	-14.6	14.1	9.7	Marine storm

References:

nr: value not reported

a) (*Monticelli, et al. 2004*), all samples glacier water at pH 7.68

b) (*Plöger, et al. 2005*), all samples from high altitude lakes at pH 7.8

c) (*Witt and Jickells 2005*), all samples are rainwater at pH 7.8

2.6 STATISTICS

Statistical tools are vital to analyzing and interpreting data sets. Improper use of statistics can lead to faulty interpretations of data. Some common statistical procedures, as well as their inherent assumptions and limits of inference are discussed in the following section.

2.6.1 Inferences and Assumptions

There are two primary types of statistical studies: randomized experiments and observational studies. In a randomized experiment, the researcher is able to randomly assign treatments to different groups in a study. An example of a randomized experiment would be a medical study where patients are randomly assigned to take two different types of medicine. In an observational study, the researcher has no control over the treatment of groups in a study. The present work is an example of an observational study – we have no control over how much rain/traffic/etc. is applied to the stormwater samples. This distinction is important in regards to the scope of inference. It is impossible to draw causal conclusions in an observational study from statistical analysis alone. There is always a possibility of confounding variables – variables that are associated to both group assignment and the outcome – affecting the measured outcome of a study. This study may only determine differences in groups and associations with explanatory variables. Significant outcomes may support, but cannot prove, causation (*Ramsey and Schafer 2002*).

Using the t -tools to analyze data from different sample groupings requires meeting three assumptions:

1. Samples must be drawn from normally-distributed populations.
2. The standard deviations of the sample measurements from different groups must be equal.
3. The observations within a sample group are independent, and the sample groups are independent of each other.

Data transformations can help in achieving normal distributions and equal variance. Additionally, the t -tools are robust in detecting departures from normality, provided the sample size is large enough (*Ramsey and Schafer 2002*). Potentially most problematic of these assumptions in a stormwater study is that of independence. The samples should be independent from each other, as a departure from this would mean that a measured outcome (response variable) is dependent on another measured outcome and not solely on explanatory variables. There is a possibility of serial correlation of samples taken at minimal temporal differences. There is also a possibility for spatial correlation between samples.

Linear regression is used when the groups in a study are not discrete, but continuously distributed over a range of values. The group becomes the explanatory variable, while the observation means become the response variable. As their name suggests, the explanatory variables aim to quantify the response variable. Simple linear regression is defined by a single explanatory variable, while multiple linear regression (MLR) is defined by two or more

explanatory variables predicting a single response variable. The assumptions necessary in a simple linear regression model are similar to those described for comparison between sample groups. They are:

1. The plot of response means as a function of the explanatory variable is a straight line.
2. The deviation of responses at different values of the explanatory variable is equal across all levels of the explanatory variable.
3. The subsets of responses at different explanatory variable values are normally distributed.
4. The response must be independent of other responses – its mean value may only be predicted as a function of explanatory variables.

In terms of MLR, ideally, the variance of a response variable should be constant over all levels of predictor variables.

2.6.2 Sample Comparison

To determine the level of significance between sample types or locations, the means of the groups of interest must be compared. To do this, a test statistic must be quantified – in this case a difference between the mean values of each sample group. Hypothesis testing then addresses the question of the level of significance in the difference of the mean of the groups. A typical hypothesis test might be concerned with proving or disproving the null hypothesis that the difference in mean measurements between two groups is zero. This analysis produces a p-value, which is a probability value that measures the uncertainty associated with the measured test statistic.

The t -tools are useful in terms of comparing samples. Using the t -tools requires computing a test statistic (t -statistic). The calculation of the t -statistic is shown in the equation below (*Ramsey and Schafer 2002*).

$$t - statistic = \frac{(\bar{Y}_2 - \bar{Y}_1) - [Hypothesized\ value\ for\ (\mu_2 - \mu_1)]}{SE(\bar{Y}_2 - \bar{Y}_1)}$$

In the above equation, \bar{Y}_2 and \bar{Y}_1 represent the sample means for groups 2 and 1, respectively; μ_2 and μ_1 represent the true means for groups 2 and 1, respectively; and $SE(\bar{Y}_2 - \bar{Y}_1)$ is the standard error of the difference between the two sample means. The hypothesized value for $\mu_2 - \mu_1$ is zero, when testing the null hypothesis of no difference between the means of the groups.

In an observational study, a permutation distribution of the t -statistic is built to calculate the p-value. This permutation distribution represents the measurement of the test statistic if the groups were randomized (and of a proper size) (*Ramsey and Schafer 2002*). The proportion of these randomized groupings that meet or exceed the observed test-statistic (i.e., the difference of means) yields a p-value. Since the “true mean” of any sample measurement can never be

quantified, and the actual measurements are only representative of that true mean, there can never be 100% certainty that there is a difference in the means of sample groups. For example, a p-value of 0.043 signifies a 4.3% possibility that the true mean of different groups is the same, and conversely, a 95.7% chance that there is a difference in the true means of the groups. A two-sided t-test examines the possibility of a t -statistic being either higher or lower than the null hypothesis value (typically zero), while a one-sided t-test is only concerned with one of those possibilities.

Confidence intervals expressing the difference in means are constructed in the general format expressed in the following equation below:

$$(\bar{Y}_2 - \bar{Y}_1) \pm M \times SE(\bar{Y}_2 - \bar{Y}_1)$$

Here, $(\bar{Y}_2 - \bar{Y}_1)$ represents the estimate of difference between groups 2 and 1, $SE(\bar{Y}_2 - \bar{Y}_1)$ is the standard error of that estimate, and M is a multiplier. In the comparison between two samples, M is a percentile of the t -distribution based on the degrees of freedom and the prescribed confidence level.

Multiple comparisons can be done on samples collected from many different groups. If comparisons between groups are planned prior to the study, the researcher should control for individual (pair-wise) confidence levels. If comparisons are unplanned, the researcher should control for an overall (family-wise) confidence level. In planned, pair-wise, comparisons, the above equation may be used with a t -value as the multiplier. Family-wise comparisons control for an overall confidence level for all comparisons (i.e., an overall confidence level that *all* comparisons between any two groups are significant). Family-wise comparisons use a variety of different procedures to determine the value for M , including Tukey-Kramer, Scheffe, and Neuman-Keuls, among others (*Ramsey and Schafer 2002*).

2.6.3 Multiple Linear Regression (MLR)

Simple linear regression models are of the form displayed in the equation below (*Ramsey and Schafer 2002*):

$$\mu\{Y | X\} = \beta_0 + \beta_1 X$$

The meaning of this equation is that the mean of the response variable, Y , can be predicted by a linear relationship with the explanatory (or predictor) variable, X . The two statistical parameters, β_0 and β_1 , represent the intercept and slope of this model, respectively. β_1 is the parameter of most concern, as it quantifies the relationship between the response and explanatory variables. MLR differs from simple linear regression by the inclusion of two or more explanatory variables, an example of an MLR model is shown below:

$$\mu\{Y | X_1, X_2, \dots, X_n\} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_n X_n$$

In this equation, the parameters β_1 thru β_n quantify the relationship of explanatory variables X_1 thru X_n with the response variable Y , respectively. Other forms of this equation are possible in MLR. For example, equations involving squared terms of an explanatory variable or multiplicative “interaction” terms of explanatory variables are also possible. Similar to sample comparison, t -statistics can be used to quantify statistical parameters (β -values). These β -values are still associated with p-values measuring the confidence of a particular β being different from zero.

2.6.4 Modeling

Building an MLR model is helpful in determining the importance of explanatory variables. One common way to do this is by using a one-way analysis of variance (ANOVA) F-test. In this test, two models are compared: the full and reduced models. The full model contains more explanatory variables than the reduced model. The fitting of these two models to a response variable produces an F-statistic, as defined below:

$$F = \frac{[SS_{res}(red) - SS_{res}(full)] / [df(red) - df(full)]}{SS_{res}(full) / df(full)}$$

The SS_{res} values are the residual sums of squares produced by a model. Large residual sum of squares measurements imply a high degree of variation between measured and modeled values. The degrees of freedom for each model (df) refers to the number of statistical parameters (β -values) subtracted from the number of observations. Notations for *red* and *full* refer to the reduced and full models being tested, respectively. Therefore, the number of degrees of freedom from the reduced model is always less than that of the full model. The F-statistic that is calculated produces a p-value based on its specific F-distribution. A large F-statistic produces a small p-value. A small p-value implies a low probability that the statistical parameter(s) included in the full model, as opposed to the reduced model, are zero. Statistical parameters can be analyzed one-by-one with ANOVA. This is different from the t -test, which produces p-values for the inclusion of a parameter after all other parameters have been accounted for.

Sometimes many different explanatory variables may have an unknown association to a particular response variable. In this situation, model variable selection can help determine key parameters in a model. A good MLR model should not be biased or overfit. A biased model does not contain enough predictor variables and therefore does not accurately account for effects of the explanatory variables in the model. An overfit model has problems of lack of power or precision (due to too few degrees of freedom), and multicollinearity – when two or more predictors have a linear relationship between each other. When two predictors have a linear relationship with each other, they are not simultaneously significant in determining the response variable.

There are various statistics that can be calculated to compare models. R^2 and adjusted R^2 can be used in model selection, but both of these statistics favor models with too many variables (Ramsey and Schafer 2002). More commonly used variable selection statistics include the Cp

statistic, Akaike's Information Criterion (AIC), and Schwarz's Bayesian Information Criterion (BIC). All of these statistics involve terms which account for the variability in the model, as well as "penalties" for models using too many predictors (*Ramsey and Schafer 2002*).

There are various approaches to model variable selection. Stepwise regression involves selectively adding or subtracting explanatory variables until the model is optimized. Stepwise regression can be done in forwards, backwards, or both-way directions. Forwards regression begins with a minimum model and adds variables one-by-one until the model cannot be further improved by the addition of more variables (based on some specified statistic, like C_p). Backwards regression starts with a full model – one which contains all possible predictors – and removes predictors one-by-one until the model cannot be improved. Two-way stepwise regression selectively adds or subtracts explanatory variables from a specified starting point. Another approach is to use best subsets variable selection. All possible predictors in the model are combined in all possible ways and a model-fitting statistic is calculated (most commonly C_p) for each combination. The user then decides on the best fit model.

Making inferences about coefficients found from the dataset used for variable selection should be avoided. Often in MLR, explanatory variables are correlated, and interpreting their regression coefficients can be difficult. The central difficulty of interpreting regression coefficients in large models is that a single explanatory variable typically doesn't change while all other explanatory variables stay constant – one predictor usually won't change in isolation (*Ramsey and Schafer 2002*). Variable selection techniques are useful in situations where many explanatory variables exist, and quantifying the effect of each is less important than noting that there is an effect.

2.7 CHEMICAL EQUILIBRIUM MODELS

Chemical speciation calculations involve solving simultaneous sets of equilibrium and mass balance equations; such problems are tedious and difficult to solve by analytical or graphical procedures. Computer programs, such as Visual MINTEQ or MINEQL+, have been developed to rapidly solve aquatic equilibrium problems. Users supply information regarding the makeup of the aquatic system, and the appropriate set of equations is solved numerically within the model that contains a database of thermodynamic information.

As stated previously, complexation reactions between organic ligands and cations are much more difficult to describe than those with inorganic ligands. Dissolved organic matter (DOM) consists of a collection of large organic molecules containing a variety of functional groups and conformations. Even the general characteristics of DOM in natural waters vary by region (*Dobbs, et al. 1989*). Therefore, accurately quantifying the ability of DOM to complex cations is difficult.

There are two general approaches to modeling DOM-cation interactions: discrete ligand models and continuous distribution models. In the discrete ligand approach, a small number of ligands (usually five or fewer) are defined to represent binding sites on DOM (*HydroGeoLogic and Allison Geoscience Consultants 1998*). Most notable of the discrete ligand models are those developed by Tao (*1992*), Tipping and Hurley (*1992*), Westall (*1995*), and Gustafsson (*2001*).

Continuous distribution models express the heterogeneity of binding sites by correlating site abundance and binding affinity. The most commonly used continuous distribution models are the NICA-Donnan model (*Benedetti, et al. 1995*) and the Gaussian DOM model (*Susetyo, et al. 1991*). A number of DOM models are available in the Visual MINTEQ program; these include:

- 1) Gaussian Model
- 2) Nonideal Competitive Adsorption (NICA)-Donnan Model
- 3) Stockholm Humic Model (SHM)

Gaussian DOM modeling assumes concentrations of individual ligands of a complex DOM mixture to be normally distributed with respect to their logK values (*HydroGeoLogic and Allison Geoscience Consultants 1998*). Site preference for specific metals varies from DOM to DOM, but each DOM molecule is assumed to have the same number of sites available (thus site distribution is split amongst metals) (*Grimm, et al. 1991*). Binding strengths of the different sites can be modeled as uni-, bi-, or tri-modal Gaussian distributions. Mathematically, the uni-modal Gaussian DOM model is described by the following equation:

$$C_i = \frac{C_L}{\sigma\sqrt{2\pi}} \exp \left[-0.5 \left(\frac{\mu_M - \text{Log}(K_{M_i})}{\sigma} \right)^2 \right] d \text{Log}(K_M)$$

In this equation, C_i is the concentration of binding site i , C_L is the total concentration of ligands, K_{M_i} is the stability constant for a specific metal M binding to ligand site i , μ_M is the mean of all $\text{Log}(K_{M_i})$ values, and σ is the standard deviation of the distribution. These parameters are visually presented in Figure 2.2. As the figure notes, at an arbitrarily high number of total binding sites (i_{\max}), $d \text{Log}(K_M)$ is equal to $(8\sigma)/i_{\max}$ (*Susetyo, et al. 1991*).

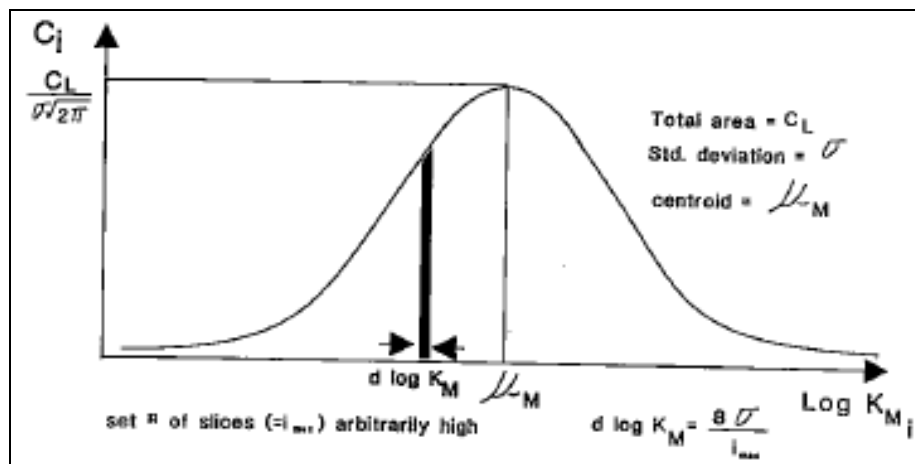


Figure 2.2: Gaussian distribution model and its important parameters (*Susetyo, et al. 1991*)

The NICA-Donnan model is a combination of the NICA cation-humic binding model and the Donnan nonspecific humic binding model (*Kinniburgh, et al. 1996*). The NICA model assumes that all sites are monodentate (one cation per site, irrelevant of charge), and that only two types of sites exist: carboxylic and phenolic (*Benedetti, et al. 1995*). The sites themselves are assumed to be continuous (*Benedetti, et al. 1995*). Non-ideality is accounted for on an ion-specific basis (*Benedetti, et al. 1995*). The Donnan model is included to account for electrostatic effects by assuming that humic material can be modeled as electrically neutral with a specific volume and average electrostatic potential called the Donnan potential (*Kinniburgh, et al. 1996*). Ionic strength has been shown to affect Cu-humic binding, but the magnitude of the effect may be due more to differing types of DOM (fulvic acid from Suwannee River, purified peat humic acid, etc.) (*Kinniburgh, et al. 1996*).

Unlike the NICA-Donnan and Gaussian models, the SHM is based on discrete metal/proton binding sites (*Gustafsson 2001*). Additionally, cations can form bidentate as well as monodentate complexes. SHM is primarily an empirically based model that assumes the NOM are impermeable spheres. The Basic Stern Model (BSM) is utilized to correct for electrostatic effects. Both SHM and NICA-Donnan model showed little effect of ionic strength on copper speciation and an underestimation of $\text{Cu}^{2+}/\text{H}^+$ exchange stoichiometry (*Gustafsson 2001*; *Kinniburgh, et al. 1996*).

3.0 METHODS

3.1 STORMWATER SAMPLING

Samples analyzed for this study included a variety of samples collected by the OSU Environmental Engineering lab, as well as composite samples collected and sent to OSU by Herrera Environmental Consultants. While the present study focuses on copper speciation in highway runoff, Herrera was working on another ODOT-funded study to characterize highway runoff water quality. Grab, first flush, and flow-weighted samples were collected at the Dixon Outfall site in Corvallis, Oregon from October 2008 through October 2009; and flow-weighted composite samples were collected and sent to the OSU lab by Herrera Environmental Consultants from March 2008 through May 2009. These composite samples arrived from sites in Portland, Wemme, and Bend, Oregon. These three sites are henceforth referred to as the “Herrera sites”. All aerial views of the sampling sites shown in the Site Descriptions section were found using Google Maps (*Google 2009*). The annotated stars indicate the approximate sampling location.

3.1.1 Site Descriptions

3.1.1.1 Dixon Outfall

Dixon Outfall is located off of Highway 20 just north of downtown Corvallis (mile point 0.75). The annual average daily traffic (AADT) of this site is approximately 8,000 (*ODOT 2008*). Three storm drains, located on the southeast curb of Highway 20, feed a 12” concrete outfall pipe which drains to Dixon Creek just upstream of where it discharges to the Willamette River. The approximate street area feeding this site is 451 m² (4,850 ft² or 0.11 acres). Precipitation measurements were taken on site with an ISCO 674 rain gauge. Figure 3.1 displays an aerial view of the area surrounding the Dixon Outfall site. The immediate vicinity of the site is residential, though the Corvallis Wastewater Treatment Plant is located nearby.

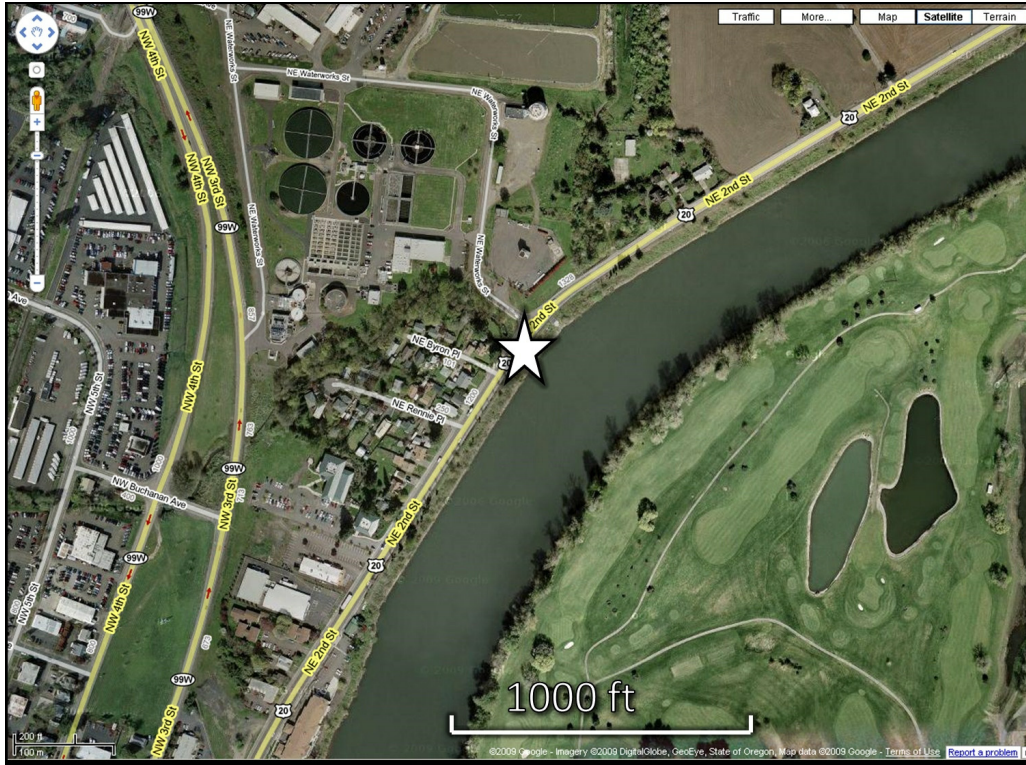


Figure 3.1: Dixon site aerial view

3.1.1.2 I-5 Convention Center

This site is located in Portland in a manhole in the Oregon Convention Center Exhibitor Parking area just west of NE 1st Avenue. The site has an AADT of approximately 130,000 and drains directly to the Willamette River through a 36” concrete pipe. The drainage area is approximately 9.4 hectares (23.1 acres) and covers a 1.55 km (0.96-mile) stretch of the I-5 corridor. Precipitation measurements were taken approximately 0.5 miles from the site at the Portland Fire Bureau Rain (55 SW Ash Street) (*Herrera Environmental Consultants 2008-2009*). Figure 3.2 displays an aerial view of the area surrounding the Portland/I-5 site and emphasizes the urban nature of this site in comparison to the other sampling sites.

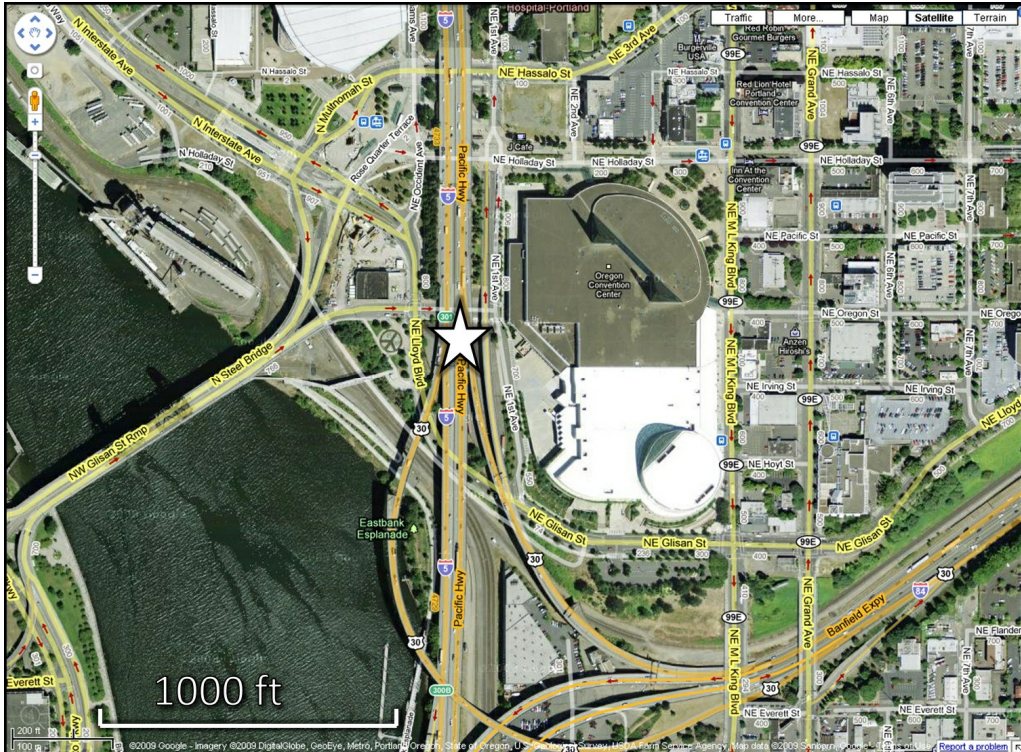


Figure 3.2: Portland/I-5 site aerial view

3.1.1.3 Bend

The Bend site is located on the north side of Highway 20, about 1.2 miles east of the Highway 20/Highway 97 intersection. The AADT of this site is approximately 24,000. A detention pond collects the roadway runoff via an 18" corrugated plastic pipe. The drainage area is approximately 0.6 hectares (1.4 acres) and covers a 0.19 km (0.12-mile) stretch of Highway 20. Precipitation measurements were obtained from a rain gauge owned by the City of Bend located across the street from the site. Figure 3.3 displays an aerial view of the area surrounding the Bend sampling site. As can be seen in this figure, the Bend site is not rural in the strictest sense. The highway AADT and the proximity to large areas of pervious, natural surfaces are both consistent with it being classified as non-urban.

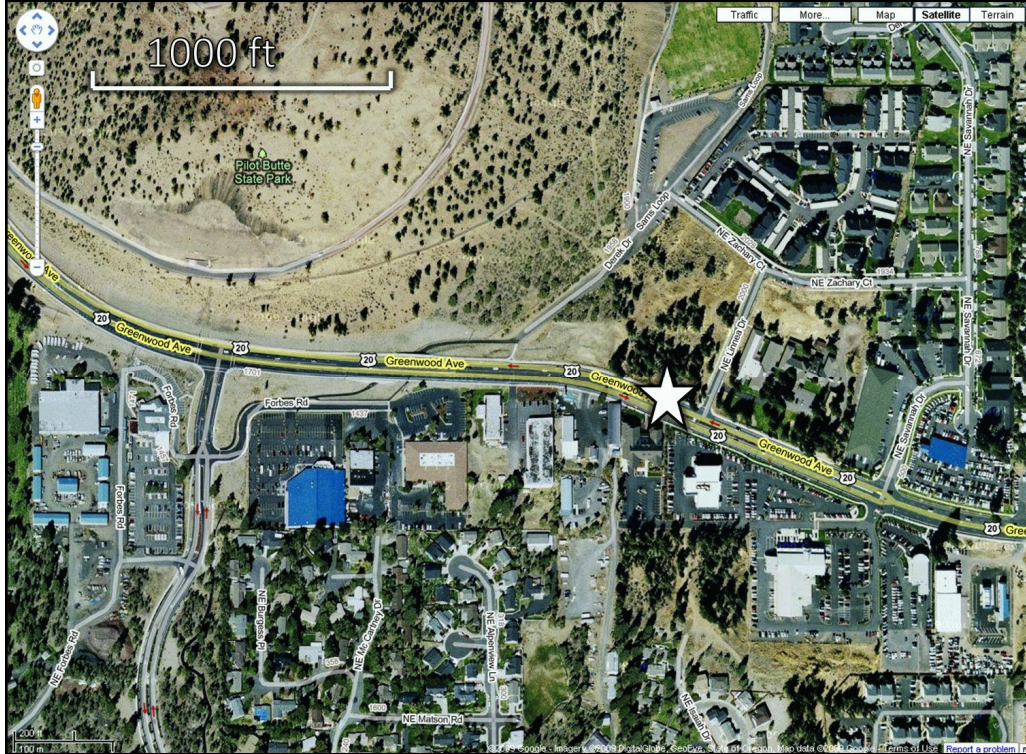


Figure 3.3: Bend site aerial view

3.1.1.4 *Wemme*

The Wemme site is an outfall located approximately 0.45 miles northwest of the Welches Road interchange north of Highway 26. The AADT of this site is approximately 12,000. The outfall is a 24” diameter, tar-lined corrugated steel pipe that drains to the Sandy River through a grass field. The drainage area is approximately 8.7 hectares (21.5 acres) and covers 1.36 miles of Highway 26. Precipitation measurements were taken from the Welches rain gauge (CW 6318), part of the Citizen Weather Observer Program (CWOP). Figure 3.4 displays an aerial view of the area surrounding the Wemme site. The immediate vicinity is forested and distant from any urban centers.



Figure 3.4: Wemme site aerial view

3.1.2 Sampling Criteria

Storm events had to meet certain criteria for the data to be considered valid. These preset criteria differed between the Dixon Outfall site and the Herrera sites. At Dixon Outfall, a storm event was considered valid if there was over 0.1” of rain occurring over a 72-hour period preceded by a 72-hour dry period receiving less than 0.1” of rain (*USEPA 1992*). Typically, the rainfall accumulated in periods of less than 24 hours. Forecasts and expected rainfall amounts were taken from the National Weather Service website (www.weather.gov). Antecedent dry periods were calculated from data at the MAR754 weather station provided by APRSWXNET and found at the Weather Underground website (www.wunderground.com).

At the Herrera sites, a storm event was considered valid if 0.15” of rain occurred over a 24-hour period preceded by a dry period receiving less than 0.04” of precipitation over six hours. The Herrera samples also specified a minimum storm duration of one hour and defined the end of a storm as a six-hour period receiving less than 0.04” of precipitation following the event.

3.1.3 Sampling Equipment/Setup

At all sites, flow-weighted samples were collected. All three Herrera sites had similar sampling setups. A Sigma 950 Bubbler Flow Meter measured water level in a pipe (converted to flow with Manning’s Equation) and triggered a portable autosampler (Sigma 800 at I-5 and Bend,

Sigma SD900 at Wemme) to take 100 ml sub-samples at a preset flow increment into one composite sample. A 3/8" inner diameter Teflon tube was used for the intake line. Figure 3.5, Figure 3.6, and Figure 3.7 show the in-pipe installations of the intake and bubbler tubes for the Portland, Wemme, and Bend sampling sites, respectively (pictures courtesy of Herrera).

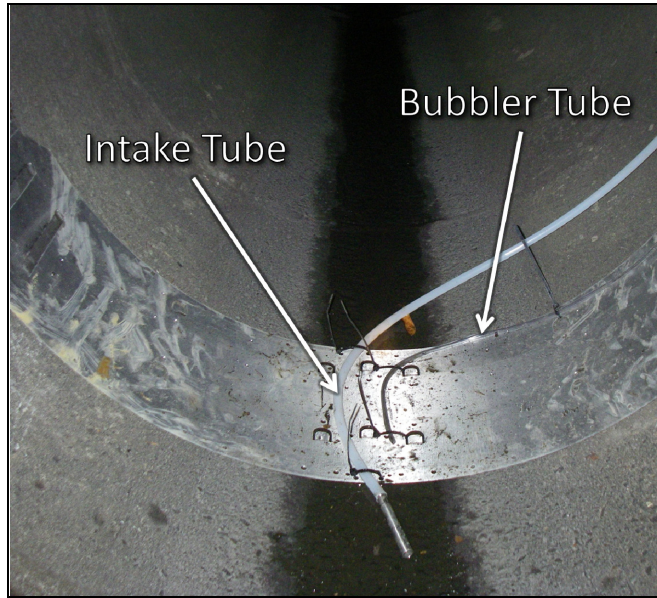


Figure 3.5: Portland/I-5 site pipe installation

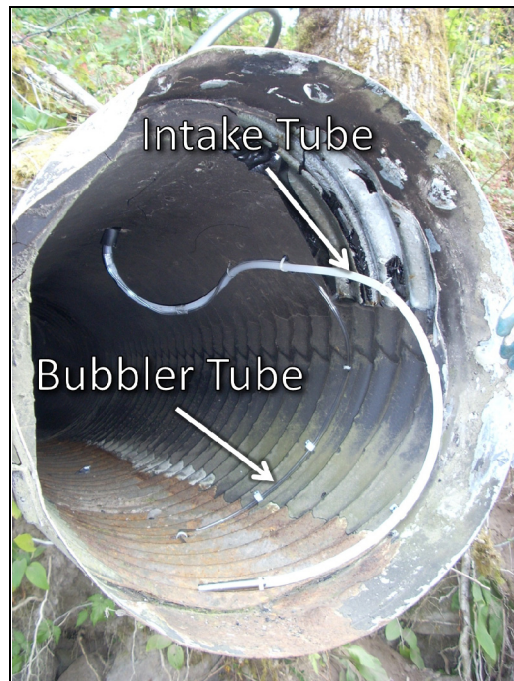


Figure 3.6: Wemme site pipe installation

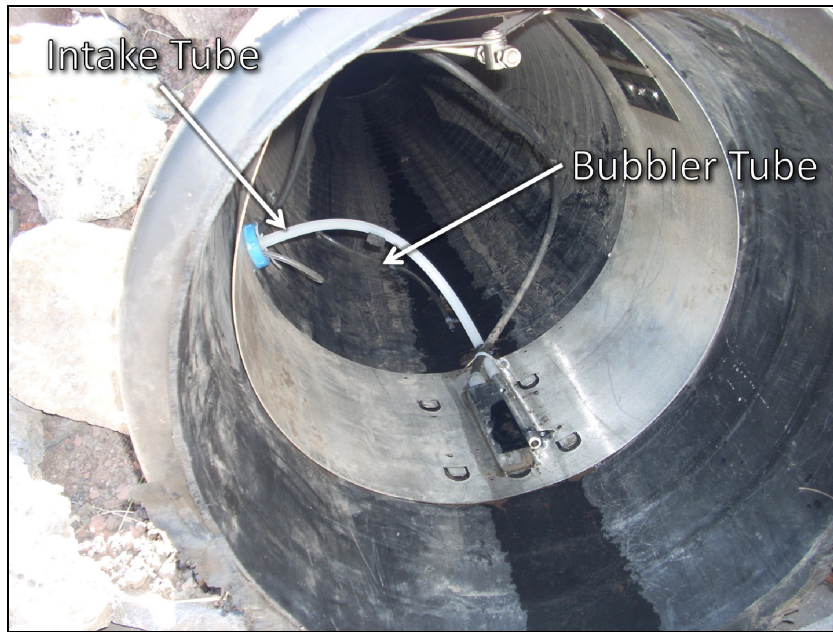


Figure 3.7: Bend site pipe installation

At the Dixon Outfall site, an ISCO 6712 Autosampler was used to collect samples into 24 separate bottles. An ISCO 730 Bubbler module and ISCO 674 Rain Gauge were both connected to the Autosampler. The bubbler reported water levels to the nearest 0.001 ft and the rain gauge recorded every 0.01" of rain. The intake line was a 25-foot, 3/8" inner diameter Teflon tube. The intake line was connected to a small piece of tygon tubing equipped with a Teflon-coated strainer on the end to collect samples. A 12" Thel-mar V-notch weir was placed at the end of the pipe to create submerged conditions. These conditions allowed for accurate level measurement and created a sufficient stormwater volume from which to collect samples. This installation is shown in Figure 3.8.

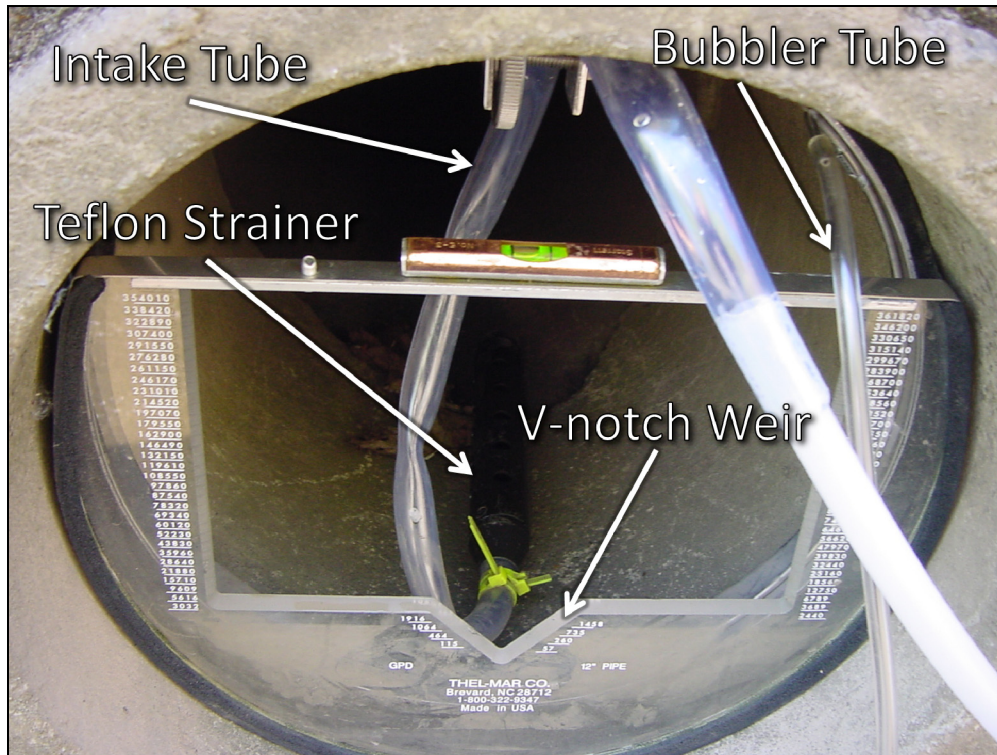


Figure 3.8: Dixon Outfall site pipe installation

Measured flow levels were converted to flowrates using the V-Notch Weir equation (*Walkowiak 2008*). This was programmed into the sampler with an 8-point calibration curve, as it was shown to give more reliable results than the manufacturer-programmed V-notch weir equation. Data for level, precipitation, and sampling events was typically recorded in 1-minute data intervals. ISCO Flowlink (v. 5.1) software was used to upload the data to a computer. Storm data was analyzed and graphed using Microsoft Excel.

3.1.4 Field Sampling Procedures

3.1.4.1 Dixon Outfall

Prior to sample collection at the Dixon Outfall site, the Teflon intake tubing was rinsed successively with acid and distilled and deionized (DDI) water (Barnstead NANOpure II system). 2 L of 10% HCl were drained through the tube followed by 2 L of 10% HNO₃. Finally, the tube was rinsed out with at least 2 L of DDI water before being taken into the field. Sample intake volume calibration was performed in the field with laboratory grade deionized (DI) water. The bubbler level was calibrated at zero in the field also using DI water.

The sampling program consisted of two parts: an initial level-triggered program, and a flow-dependent program. The first part of the program was designed to take one 950-mL sample at the first level measured above 0.12". This part of the program collected the

“first flush” samples from the storms. The second part of the program was based only on flow-pacing and initiated directly after the first part completed. This part of the program produced discrete 950-mL samples at points throughout the storm after a certain volume of flow passed by. Flow pacing for this sampling was determined based on the expected rainfall and the desired number of bottles to be filled – i.e., larger storms would be paced at larger flow volumes.

Sampling bottles were uncapped with gloved hands directly prior to sampler setup. The caps were stored in a new re-sealable plastic zipper bag until they were needed to recap the bottles. The central cavity in the autosampler was filled with ice to keep the samples cool. After sample collection, the sample bottles were recapped with gloved hands immediately after the sampling program was stopped. Field blanks – consisting of DDI water sampled through the Teflon intake tube and into an open container inside the sample – were taken for some storms.

3.1.4.2 Herrera Sites

At the Herrera sites, autosamplers and other field equipment were installed semi-permanently, as opposed to the Dixon Creek installation, which was set up for each sampling event. Immediately following equipment installation, field personnel calibrated sample aliquot volumes. One week after the field equipment was installed field personnel visited each site to confirm that it was installed correctly and functioning as designed. The field equipment was checked routinely to gather data, replace batteries (when necessary), visually inspect system components, and perform calibration checks as necessary (*Herrera Environmental Consultants 2008*).

Once a potential storm event was targeted for sampling, field personnel visited each station to verify the proper function of the autosampler, install a clean 15.2-liter polyethylene carboy, add crushed ice surrounding the carboy, and begin the sampling program. Flow-pacing for the composite sample was determined by plotting projected rainfall totals on a rainfall-runoff rating curve, generated for each monitoring site after a sufficient amount of data was collected. After each targeted storm event, field personnel returned to the sampling site to verify the proper function of the sampling equipment and upload the sample collection data from the automated samplers to a laptop computer or a proprietary data transfer device. Carboys were then removed from the autosampler, shaken to homogenize the sample, and divided into laboratory bottles.

3.2 LABORATORY METHODS

The goals for this project included quantifying copper speciation and examining correlations for copper and copper speciation with other water quality parameters, storm characteristics, and site characteristics. In order to accomplish these objectives, a variety of analyses were performed on each sample. The flowchart shown in Figure 3.9 displays the parameters measured and the aliquot volumes needed for each determination. The first step in this process was separating the sample into ‘total’ and ‘dissolved’ subsets. Subsequently, measurements were made for total suspended solids (TSS), pH, conductivity, alkalinity, cations (both major cations and metals),

anions, total dissolved solids (TDS), dissolved organic carbon (DOC), and $\text{Cu}^{2+}_{\text{free}}$ (speciation). These procedures are detailed in sections 3.2.1 through 3.2.10.

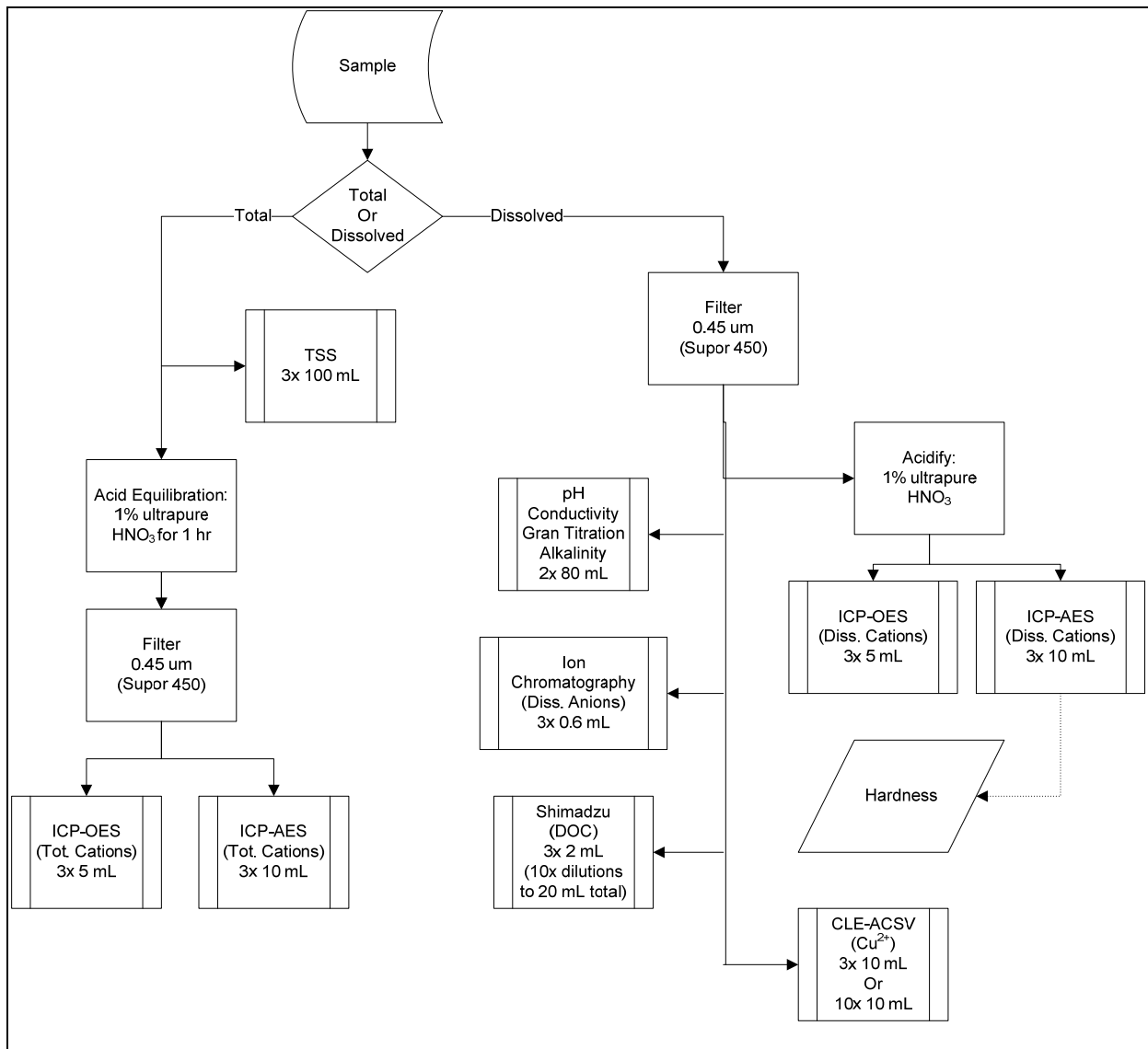


Figure 3.9: Sample processing flowsheet

3.2.1 Sample Separation

Samples collected for this study included discrete samples collected at the Dixon Outfall site in Corvallis and flow-weighted composite samples collected and sent to the OSU lab by Herrera Environmental Consultants. These composite samples arrived from sites in Portland, Wemme, and Bend; these sites are henceforth referred to as the “Herrera sites.” All sampling sites are detailed in Section 3.1.1. Samples received from the Portland and Wemme sites were separated from the bulk sample at Herrera’s Portland office. Herrera engineers first obtained enough of the

stormwater samples to analyze for their stormwater characterization study prior to pouring off an aliquot for our analysis. This separation typically occurred within one hour of sample collection at the Portland site and two hours for the Wemme site. Samples collected from the Bend site were separated within two hours of initial collection. The Herrera composite samples were delivered to the OSU lab in a cooler with ice through the mail within 24 hours of initial collection. Samples from Dixon Outfall were taken directly from the field to the OSU lab after collection. All samples were processed within 24 hours of receipt in the lab.

Clean containers and instruments were used for each step in sample analysis. Labware cleaning procedures are detailed in Section 3.2.2. Composite samples from Dixon Outfall were formed from discrete flow-weighted samples in the lab. Individual flow-weighted samples were thoroughly mixed and an aliquot was drawn out and pipetted into a new, clean container for the composite sample. The final volume of the composite sample was 800-1000 mL. The volume of the aliquots varied based on the number of flow-weighted samples taken for a specific storm. Snub-nosed volumetric pipets (to avoid excluding solids) were used to draw these aliquots. The pipet(s) were rinsed thoroughly with DDI water between uses.

Upon arrival, raw samples were immediately analyzed for total suspended solids (see Section 3.2.3). Approximately 60 mL of the raw sample was taken for analysis of total cations. In this work, “total” cations refers to the concentration of cations released after an acid addition of 1% (v/v) ultrapure HNO₃ (Aristar Ultra). The acid treatment facilitates mobilization of any cations in solid form (adsorbed or pure solid) and dropped the pH below 2. This represents a total concentration of potentially environmentally available cations. These samples equilibrated in a covered beaker for over an hour.

The aliquots for both the dissolved and total samples were vacuum-filtered with 0.45 µm filters (Pall Supor 450). Filters were stored in 1% ultrapure HNO₃ for at least one day prior to use. Filters were rinsed with 250 mL of DDI water before use. The filtrate was collected in 500- or 250- mL vacuum flasks.

After filtering, the bulk dissolved samples were stored in 1000- or 500-mL HDPE containers. Aliquots for dissolved cations and anions were transferred into appropriately sized containers, acidified (1% ultrapure HNO₃ addition), and stored in the dark at 4 °C until analysis. Aliquots for determination of DOC were transferred into appropriately prepared glass DOC bottles. Once the alkalinity was measured for the dissolved sample, the remainder was stored in a freezer (-20° C) awaiting speciation testing. Aliquots for total cations were transferred directly from the vacuum flasks to appropriately sized containers.

3.2.2 Cleaning Procedures

3.2.2.1 General Containers/Labware

Majority of labware was cleaned in successive acid baths and DDI water. Labware cleaned in this process includes glassware, HDPE containers (including autosampler bottles), and Teflon bottles (used for copper speciation measurements). This cleaning procedure is detailed below:

- 1) Particulates were removed from labware by rinsing and scrubbing with DI water.
- 2) Labware was submerged in a 10% (v/v) HCl bath for at least 18 hours.
- 3) Labware was taken out of the HCl bath and put into a 10% HNO₃ bath for at least 18 hours. Both acid baths were made with reagent grade acid and changed out every four months.
- 4) Upon removal from the HNO₃ bath, labware was rinsed off with DI water and submerged into a DDI bath for at least 30 minutes.
- 5) Each piece of labware was rinsed out three times with DDI water. Where applicable, containers were immediately capped after being rinsed out. Otherwise, labware was allowed to dry upside-down and subsequently covered with Parafilm.

3.2.2.2 Organic Carbon Bottles

After use, organic carbon bottles were rinsed with DI water. The bottles were then soaked in a 10% HCl bath for at least 24 hours. Upon removal from the acid bath, the bottles were rinsed thoroughly with DI water and allowed to dry. Finally, the bottles were ashed at 550°C in a muffle furnace for at least two hours and subsequently stored in a closed container.

3.2.2.3 Organic Carbon Septum Caps

After use, the organic carbon bottle septum caps were rinsed twice with DDI water and stored in a re-sealable plastic zipper bag filled with DDI water for at least 24 hours. At the end of this time, they were rinsed three more times with DDI water and allowed to dry. They were then stored in a re-sealable plastic zipper bag.

3.2.2.4 Voltammetric Teflon Cup

The Teflon cup used in speciation measurements was filled with 1% Ultrapure HNO₃ until needed. Prior to use in voltammetric determinations, the cup was emptied and rinsed thoroughly with DDI water.

3.2.3 Total Suspended Solids (TSS)

TSS was measured in accordance with Standard Method 2540D (*APHA, et al. 2005*). Typically, aliquots of 80-110 mL of the sample were used in this determination. TSS determinations were performed in triplicate.

3.2.4 pH and Conductivity

75-90 mL of dissolved sample was used to measure initial pH, conductivity and alkalinity. Initial pH was measured with a VWR symphony probe and an Accumet AR50 control panel. The pH probe was calibrated daily with pH buffers of 4, 7, and 10 (BDH General). Conductivity was measured on the same control panel with an Accumet conductivity probe. Conductivity was standardized with a 970 $\mu\text{S}/\text{cm}$ solution. Typically, pH and conductivity determinations were done in duplicate.

3.2.5 Alkalinity

The same 75-90 mL aliquot of dissolved sample used for pH and conductivity measurements was used for alkalinity determination. Alkalinity was measured with a Gran Titration using 0.01 M (0.02 N) sulfuric acid. The theory behind this method is described in Stumm and Morgan (1996).

3.2.6 Cations

Total and dissolved cation concentrations were analyzed with Inductively Coupled Atomic Emission Spectrometry (ICP-AES) (Standard Method 3120), and either Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Standard Method 3125) or Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). All cation concentrations were measured within 6 months of sample collection. ICP-AES was used to quantify Ca, Mg, Fe, Pb, Cd, Cu, Zn, K, Ni, Na at levels above 50 ppb. 10 mL of sample was required for each ICP-AES measurement and samples were run in triplicate. Samples were stored in HDPE or glass containers. ICP-MS was used for Pb, Cd, Cu, Zn, and Ni below the 50 ppb concentration. ICP-OES was used for Fe, Cu, Pb, Cd, Ni, and Zn between the 1 ppb (higher for Pb, Ni, and Cd) and 200 ppb levels. 5 mL of sample was required for either ICP-MS or -OES and samples were run in triplicate. Samples measured on the ICP-MS or -OES were stored and capped in single-use BD Falcon polypropylene conical test tubes.

Standards were made from single element ICP Standards (BDH; Aristar). For the ICP-MS, an internal standard was added to each sample (2 ppb Indium). DDI blanks with a 1% ultrapure HNO_3 addition were used with ICP-MS, -OES, and -AES. Multiple-point calibration curves for cation measurements were constructed from known standards at the concentrations listed in Table 3.1.

Table 3.1: Concentrations used for cation calibration curves

TEST METHOD	UNITS	CONCENTRATIONS
ICP-AES	mg/L (ppm)	0.05, 0.08, 0.16, 0.50, 1.0, 5.0
ICP-OES	$\mu\text{g}/\text{L}$ (ppb)	1.0, 5.0, 10, 20, 50, 100, 200
ICP-MS	$\mu\text{g}/\text{L}$ (ppb)	0.01, 0.05, 0.20, 0.50, 1.0, 10, 50

For ICP-AES measurements, a 15 mg/L standard for Ca, Mg, and Na was also used in calibration. Due to some curvature in intensity versus concentration plots over the entire range of concentrations measured, high- and low-range calibration curves were used for each element.

Low-range calibrations measured values up to and including 0.5 mg/L, while high-range calibrations measured at 0.5 mg/L and above. At minimum, a blank and check standard were tested every 50 samples (including standards). For some tests, the entire set of standards was re-measured at the end of a sample run. Hardness was calculated from the measured Ca and Mg concentrations in accordance with Standard Method 2340 (APHA, et al. 2005).

For ICP-OES measurements, a 50 ppb check standard was measured every 17 samples. For ICP-MS measurements, the entire calibration curve was re-measured at the end of a sample run. Method blanks consisted of DDI water that underwent the filtration process.

3.2.7 Anions

Anions were measured following Standard Method 4110 (APHA, et al. 2005). 2 mL of the dissolved samples were stored in small HDPE containers and refrigerated prior to anion determinations. These samples were analyzed for nitrate, nitrite, sulfate, phosphate, and chloride (the major anions in stormwater) using a Dionex Ion Chromatograph (DX500). Each sample was measured as a 10x dilution and at full strength in order to elucidate any peak area suppression that occurred. All measurements were performed in triplicate. A set of standards made from dry chemical stock were measured alongside the samples. The standards ranged from 50 ppb to 20 ppm. Due to the large range of concentrations, the standard curves were separated into two sets – a high set used to determine concentrations from 1 ppm to 20 ppm, and a low set covering 50 ppb to 1 ppm. Blanks consisted of DDI water and method blanks consisted of DDI carried through the filtering procedure.

3.2.8 Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) were calculated from dissolved anion and cation concentrations. The mass concentration of each constituent (anion and cation) was reduced to a molar concentration and then summed. Equation (3-1) below shows the general formula used. Here, C_i and A_i represent individual cation and anion species, respectively, while x represents the charge on the species.

$$TDS = \sum_i [C_i^{+x}] + \sum_i [A_i^{-x}] \quad (3-1)$$

3.2.9 Dissolved Organic Carbon (DOC)

Dissolved organic carbon (DOC) determinations were made on a Shimadzu TOC-V_{CSH} total organic carbon analyzer at Oregon State's Institute for Water and Watersheds Collaboratory following Standard Method 5310 (APHA, et al. 2005). Samples were tested for organic carbon within a week of their receipt in the lab. Samples were stored in the dark at 4°C prior to analysis. Typically, samples were run at a 5X or 10X dilution with DI water from the Collaboratory. Calibration curves were constructed from standards of 0, 0.2, 0.5, 1.0, 2.0, and 5.0 mg/L of organic carbon. Standards were made at the Collaboratory with potassium hydrogen phthalate as the source of organic carbon.

3.2.10 Copper Speciation Measurements (CLE-ACSV)

An alteration of the CLE-ACSV method described in Campos and van den Berg (1994) was used for determination of α_{CuSAx} . A modified version of CLE-ACSV method from Buck and Bruland (2005) was utilized for copper speciation. Important differences in the CLE-ACSV methodology developed for seawater and the methodology developed in this study for stormwater are the selection of pH and ionic strength.

For both α_{CuSAx} determinations and copper speciation experiments the pH was adjusted to 6.80 to reflect ambient pH for stormwater in this study (6.78±0.3). This change was made in order that ligand concentrations, associated stability constants, and the Cu^{2+}_{free} concentrations would be as similar as possible to actual values while still allowing for comparison between the sites. α_{CuSAx} values are specific to pH and ionic strength and therefore a constant pH (and ionic strength) was important to maintain across samples.

The dependency of α_{CuSAx} values on ionic strength required an ionic strength adjustment for the stormwater samples to a (quasi) constant value to compensate for the highly variable ion concentrations from storm to storm and site to site. A minimum ionic strength value of 0.05 M was chosen to mitigate varied ionic strengths ranging from 0.003 to 0.016 M. A second result of increasing ionic strength is an enhancement to the sensitivity of the method. This adjustment boosted the sensitivity in stormwater grab samples in preliminary studies by ~3 times.

3.2.10.1 Reagents

All samples tested with CLE-ACSV were buffered to pH 6.8 with a 1M PIPES (Piperazine-N,N'-bis(2-ethanesulfonic acid)) standard made with PIPES (J.T. Baker) in DDI. Minor pH adjustments were made with ultrapure NH_4OH (BDH Aristar Ultra) and HNO_3 (BDH Aristar Ultra) diluted in DDI. Ionic strength adjustments were done with a 5 M NaCl standard made with ultrapure NaCl (Alfa Aesar Puratronic) in DDI. Copper and Calcium standards were made from ICP standards (BDH Aristar Plus, EMD Certipur) diluted with DDI where necessary. 1 mM ethylenediaminetetraacetic acid (EDTA) standards were made from Na_2EDTA (J.T. Baker) in DDI; 50 and 500 μM EDTA standards were made from subsequent dilutions with DDI. 10 mM SA standards were made with Salicylaldehyde (Alfa Aesar) in 100% Methanol (BDH); 1 mM SA standards were made by dilution with DDI and changed biweekly.

3.2.10.2 Determination of α_{CuSAx}

α_{CuSAx} was determined by calibration through titration with a known ligand. Identical to Campos and van den Berg (1994), ethylenediaminetetraacetic acid (EDTA) was selected as the known ligand of choice. A bulk solution was made containing DDI, 100 nM of copper, 5 mM PIPES, varying calcium concentrations (1, 10, 50 ppm) and enough NaCl to adjust the ionic strength to 0.05 M. Clean Teflon bottles were conditioned by leaving 10 mL aliquots of this solution to soak for 30 minutes. After conditioning, a second 10 mL aliquot of the solution was placed in each conditioned bottle with a variable addition

of EDTA (0 to 6 μM) and allowed to equilibrate overnight. SA was added 15 minutes before each sample was analyzed in a Teflon voltammetric cup that had been previously conditioned with SA. α_{CuSAx} was determined using the following equation (Campos and van den Berg 1994):

$$\alpha_{CuSAx} = \left[\frac{(\alpha_{Cu'} + \alpha_{CuEDTA})X - \alpha_{Cu'}}{1 - X} \right] \quad (3-2)$$

Where, $\alpha_{Cu'}$ is the alpha coefficient for inorganic complexes, described in full by Equation (3-3); α_{CuEDTA} is the alpha coefficient for the copper-EDTA complex, described by Equation (3-4); and X is the ratio describing the reduction in peak current, i_p , in the presence of EDTA described by Equation (3-5) (Campos and van den Berg 1994).

$$\alpha_{Cu'} = 1 + \sum_i \left(\beta'_{CuX_n} [X'_i]^n [Cu_{free}^{2+}] \right) + \sum \left(\beta'_{CuOH_n} \frac{[Cu_{free}^{2+}]}{[H^+]^n} \right) \quad (3-3)$$

$$\alpha_{CuEDTA} = K'_{CuEDTA} [EDTA'] \quad (3-4)$$

Where K'_{CuEDTA} is the conditional stability constant for the copper-EDTA complex for a specific pH and ionic strength; $[EDTA']$ represents the concentration of EDTA that is not bound by copper. α_{CuEDTA} was determined in Visual MINTEQ by iterating α_{CuSAx} values until a best fit between experimentally measured and modeled peak ratios was reached. Previous studies assumed $[EDTA'] \approx [EDTA]_T$, but this was not a reasonable assumption because the $[EDTA]_T$ used in these titrations was on the same order of magnitude as the copper additions.

$$X = \frac{i_p}{i_{p,0}} = \frac{S[Cu(SA)_2]}{S[Cu(SA)_2]_0} \quad (3-5)$$

Where $S[Cu(SA)_2]$, $S[Cu(SA)_2]_0$ represent the peak response of the solution with and without EDTA, respectively.

α_{CuSAx} was calculated from the peak ratio range of 0.1 to 0.8. This range eliminated any potential problems in distinguishing the signal from background noise at a low peak ratio (high EDTA concentration). Applying this criterion to all determinations provided consistency as well.

3.2.10.3 Total Dissolved Copper

Dissolved copper concentrations, $[Cu_{diss}^{2+}]$, for copper speciation were measured with ICP-OES/MS. Previous studies have used UV digested water and CLE-ACSV to determine ambient copper concentrations. Preliminary tests in this study using CLE-ACSV on UV digested stormwater resulted in under estimations of Cu_{diss}^{2+} concentrations in comparison to ICP measurements. The source of this difference was most likely refractory organics complexing copper.

3.2.10.4 Sample Speciation

Typically, 130 mL of each dissolved sample was set aside for copper speciation and placed in clean Teflon bottles in 10 mL aliquots. Teflon bottles were allowed to equilibrate with copper additions (0 to 600 nM), NaCl, and 5 mM of PIPES for two hours. SA additions (resulting in 2 or 10 μ M final concentrations) were made 15 minutes before being transferred to a Teflon voltametric cup and analyzed.

The first (of two) samples containing no added copper were used to condition the voltametric cup and electrodes. The Teflon cup and instrument were also conditioned (warmed-up) with a solution containing 10 or 25 μ M of SA and 5 mM PIPES until a baseline response of 1-3 nA was reached. All Teflon bottles used for speciation tests were conditioned for 30 minutes with 10 mL of DDI and an addition of copper equivalent to test conditions.

Samples under analysis were subject to the following steps: (1) 5 min nitrogen purging step to remove all oxygen while stirring at 600 rpm; (2) 10 second quiescent equilibration; and (3) a potential of -0.15 V was applied for 1 min (while stirring) to aid adsorption of $CuSA_2$ onto the mercury drop. Finally, the potential was scanned from -0.00 V to -0.60 V and a current proportional to the concentration of reduced Cu^{2+} (to Cu^0) was produced. The peak current that centered about -0.14 V was plotted against added copper concentration for each sample in the titration.

The information from the titration was used to solve Equation (2-5). For clarity purposes Equation (2-5) is simplified and reproduced here:

$$[Cu_{diss}^{2+}] = [Cu_{free}^{2+}] + [CuL] + \sum [CuX_i] + [CuSA_x] \quad (2-5)$$

$[Cu_{diss}^{2+}]$ represents the entirety copper in the system, including added copper in the titration. $[Cu_{free}^{2+}]$ represents the free ionic copper in the titration test (distinctly different from free ionic copper in the sample at normal conditions). $[CuL]$ is the concentration of copper bound to organic ligands in the system. $[CuX_i]$ represents the entirety of copper bound to inorganic ligands in the system. $[CuSA_x]$ represents the amount of copper bound to SA. $[CuSA_x]$ was determined with Equation (3-6); where i_p is the instrument

response (current) and S is the sample sensitivity. The sensitivity is equal to the linear portion of the titration plot and is described in more detail in Section 4.2.3.1.

$$[CuSA_x] = \frac{i_p}{S} \quad (3-6)$$

$[Cu_{free}^{2+}]$ was calculated with Equation (3-7).

$$[Cu_{free}^{2+}] = \frac{[CuSA_x]}{\alpha_{CuSA_x} + \alpha_{Cu}} \quad (3-7)$$

$[CuX_i]$ was calculated with Equation (3-8).

$$[CuX_i] = (\alpha_{Cu} - 1)[Cu_{free}^{2+}] \quad (3-8)$$

$[CuL]$ was calculated with Equation (2-5).

3.2.10.5 CLE-ACSV Instrument Settings

Table 3.2 lists the settings for the VA 797 Computrace from Metrohm for all CLE-ACSV tests.

Table 3.2: VA 797 Instrument settings

PARAMETER	VALUE	UNITS
Drop Settings		
Drop Size	9	--
Drop Method	HMDE	--
Deposition Settings		
Deposition Potential	-0.15	volts (V)
Deposition Time	60	seconds (s)
Equilibration Time	10	s
Sweep Settings		
Start Potential	-0.00	V
End Potential	-0.60	V
Pulse Amplitude	0.05	V
Pulse Time	0.035	s
Voltage Step	0.004	V
Voltage Step Time	0.2	s
Sweep Rate	0.02	V/s
Other Settings		
Stir Rate	600	rpm

3.2.10.6 Speciation Calculations for Stormwater

Ligand concentrations, $[L_T]$, and conditional stability constants, K'_{CuL} , were determined through non-linear least squares fits of Equation (3-9). This equation is a version of the Langmuir equation (Gerringa, et al. 1995).

$$[CuL] = [L_T] \frac{K'_{CuL} [Cu_{free}^{2+}]}{1 + K'_{CuL} [Cu_{free}^{2+}]} \quad (3-9)$$

For $[L_T] \geq [Cu_{tot}^{2+}]$, free ionic copper in stormwater samples was calculated iteratively with Equation (3-10). This equation was derived through solving Equation (3-11) for $[Cu_{free}^{2+}]$.

$$[Cu_{free}^{2+}] = \frac{[Cu_{diss}^{2+}]}{\alpha_{Cu'} + \frac{K'_{CuL} [L_T]}{1 + K'_{CuL} [Cu_{free}^{2+}]}} \quad (3-10)$$

$$K'_{CuL} = \frac{[CuL]}{[Cu_{free}^{2+}][L']} \quad (3-11)$$

3.3 STATISTICS

The S-Plus® 8.0 statistical software was used for all statistical analyses. A 95% confidence level was used for all analyses. Therefore, for significance to be shown, the p-value of a test should be less than 0.05.

Comparisons between sample groupings were made based on composite samples from different sites, first flush and composite samples from Dixon Outfall, and inter-site differences in speciation results. These comparisons were planned, so individual confidence levels are acceptable. Differences between sites were quantified by Fisher's Least Significant Difference (LSD) multiple comparison procedure. This procedure uses an F-test to first determine if any differences between any two sites are significant. If the p-value from this F-test is large (here, >0.05), no individual significant differences are determined. If the p-value is <0.05, the procedure continues by evaluating pair-wise differences using the *t*-tools.

Inferences on first flush samples were made with a simple linear regression model involving only a first flush indicator variable. An indicator variable is a binary term that indicates the group association of a particular measurement. Indicator variables are 1 when their specific association is met, and 0 in all other cases. In this case, the indicator was one for first flush samples and zero otherwise. Site indicator variables were also used in the MLR analysis examining the effects of

hydrologic parameters on $\text{Cu}^{2+}_{\text{diss}}$ in composite samples. The results of a simple linear regression using a single indicator variable are identical to a two-sample t -test.

Model variable selection was done using backwards stepwise regression. Site indicator variables were used in the analysis of hydrologic parameters. S-Plus uses the C_p statistic as a measure of goodness-of-fit (*Insightful Corporation 2007*) in stepwise regression. The C_p statistic is shown in the equation below.

$$C_p = p + (n - p) \frac{(\sigma^2 - \sigma_{full}^2)}{\sigma_{full}^2}$$

In this equation, p is the number of regression coefficients, n is the sample size, σ^2 is the residual mean square of the model being considered, and σ_{full}^2 is the residual mean square of the full model.

3.4 VISUAL MINTEQ MODEL PARAMETERS

Visual MINTEQ, version 2.5.2 was used to model chemical equilibrium speciation. This version of the software is based on MINTEQA2 version 4.0. This software uses activity corrections based on the Davies equation. Unimodal Gaussian DOM distributions were used to model DOM interactions in Visual MINTEQ. This was done to match previous work done by Dean, et al. (2005) examining metal speciation in stormwater. This model only examines the carboxylic binding sites. Default parameters from Visual MINTEQ were used in modeling cation-DOM interactions. The default μ values for the various DOM interactions with other species were taken from research by Susetyo, et al. (1991), which examined metal-humic interactions using Lanthanide Ione Probe Spectroscopy on Suwanee River DOM.

All measured dissolved concentrations chemical constituents were input into the program by the user. DOM was accounted for by entering in the measured concentration of DOC. The pH was set constant at the value analytically measured in the sample. Solids were not allowed to precipitate. None of the thermodynamic parameters in Visual MINTEQ's database were altered from their default values. The ionic strength of the solution was not set constant, but rather calculated by the program. Charge imbalance calculated by the program was typically 10-20%.

Model comparisons to analytical results for composite samples were modeled in Visual MINTEQ using three different DOM models: Gaussian, NICA-Donnan, and Stockholm Humic Model (SHM). pH, Na, and Cl concentration of the models were adjusted to reflect experimental test conditions (pH 6.80, ionic strength of 0.05M). Default model parameters were used in all models; a concise list is shown in Table 3.3, Table 3.4, and Table 3.5.

Table 3.3: Gaussian model parameters

Parameter	Value
DOM Component	DOM1
DOC Concentration	varied
Fixed Database Values	selected
Speciation Based Values	unselected

Table 3.4: NICA-Donnan model parameters

Parameter	Value
Parameter File	genFA.npf.txt
Mol H ⁺ dissociating groups, type 1	0.00588
Mol H ⁺ dissociating groups, type 2	0.00186
Donnan Vol. Parameter	0.57
Width of Distribution, type 1	0.59
Width of Distribution, type 2	0.7
nH1	0.66
nH2	0.76

Table 3.5: SHM parameters

Parameter	Value
Parameter File	Typicalfa.mpf.txt
Stern layer capacitance	2
Spherical radius	0.75
Site density	1.2
Gel fraction parameter	0.72
Conc. Type B sites	30
Central log K of type A groups	-3.51
Central log K of type B groups	-8.81
Delta-pKA	3.48
Delta-pKB	2.49
Log KC	0.8
File for SHM site settings	Default.MSI.txt

4.0 RESULTS AND DISCUSSION

4.1 TOTAL AND DISSOLVED COPPER

This study focuses on the speciation of copper in highway runoff and factors that may affect the presence and form of copper from roadways draining into surface waters. From the literature review, some of the factors likely to influence the presence of copper in runoff samples include AADT, Urban site classification, ADP, the First Flush Effect, Total Rainfall, and Rainfall Intensity. Additionally, water quality parameters will be examined for correlations with both total and free ionic copper. Of these parameters, DOC and TSS are known to complex and adsorb copper, respectively (*Allen and Hansen 1996; Buck and Bruland 2005; Gerringa, et al. 1998; Lee, et al. 2005; Stead-Dexter and Ward 2004*). Due to the ability of natural organic matter (NOM) to strongly complex copper, as discussed in Section 2.1, both dissolved copper and DOC (a surrogate measure for NOM) have been examined in some of the statistical analyses. For the purposes of data analysis, the concentrations of most constituents and hydrologic variables have been log-transformed. These transformations are common in stormwater studies (*Burton, Jr. and Pitt 2002; Kayhanian, et al. 2003*), have been used for copper concentrations (*Kayhanian, et al. 2003*), and they provided consistently better statistical distributions for most measurements in this study. For clarity, dissolved copper will be referred to as $\text{Cu}^{2+}_{\text{diss}}$, and total copper will be referred to as $\text{Cu}^{2+}_{\text{tot}}$ throughout this section.

4.1.1 Site Comparison

The overall results from the composite samples from all sites are shown in Table 4.1 (dissolved samples) and Table 4.2 (total samples). In general, the I-5 site showed consistently higher concentrations of all stormwater constituents. Also significant is the fact that the Wemme samples from 1/6/2009 and 3/16/2009 had unusually high conductivity, as well as abnormally high concentrations of magnesium (and therefore, hardness) and chloride. These outliers are likely due to the addition of magnesium chloride to the roadway surface as a de-icing chemical. The two Wemme samples in question were removed from the data set when examining correlations between copper and the above listed parameters due to their artificially high values of conductivity and hardness. Only two samples were received from the Bend site, which limits the inferences that can be made for that site.

Table 4.1: Summary of dissolved constituent concentrations in composite stormwater samples

SITES	I-5		DIXON		WEMME		BEND	
NUMBER OF SAMPLES	5		8		7		2	
PARAMETER (UNITS)	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN
General Water Quality								
• pH	6.24 – 7.15	6.92	6.26 – 7.31	6.63	6.41 – 7.04	6.80	6.66 – 6.86	6.76
• Conductivity (µS/cm)	55.2 – 141	83.9	16.3 – 48.2	23.5	18.2 – 1065	206.5	77.4 – 152	115
• Alkalinity (mg/L as CaCO ₃)	13.8 – 29.9	18.41	4.19 – 10.0	6.29	3.62 – 14.1	8.84	9.68 – 10.1	9.89
• Hardness (mg/L as CaCO ₃)	22.7 – 43.4	30.9	5.24 – 12.2	8.25	9.61 – 477	95.9	27.3 – 72.8	50.1
• TSS (mg/L)	23.1 – 118	89.9	14.5 – 162	26.1	26.6 – 117	61.8	85.8 – 241	163
• DOC (mg/L)	5.88 – 9.97	7.00	1.81 – 10.8	4.51	1.54 – 5.97	2.50	5.16 – 5.8	5.48
Major Cations								
• Calcium (mg/L)	5.96 – 11.6	9.14	1.62 – 3.51	2.46	1.64 – 21	10.9	2.72 – 4.27	3.50
• Magnesium (mg/L)	1.14 – 3.51	1.78	0.29 – 0.83	0.45	0.62 – 103	16.5	4.98 – 15.1	10.0
• Sodium (mg/L)	1.61 – 5.14	2.38	0.83 – 2.50	1.17	0.56 – 9.62	1.68	1.17 – 1.6	1.39
• Potassium (mg/L)	0.56 – 2.53	1.49	0.33 – 0.85	0.62	bdl – 0.52	0.35	0.48 – 0.74	0.61
• Iron (mg/L)	bdl	bdl	bdl – 0.059	0.031	bdl – 0.009	bdl	bdl – 0.24	NA
Anions								
• Chloride (mg/L)	2.13 – 16.7	3.52	0.77 – 3.27	1.14	2.42 – 489	40.3	17.5 – 55.8	36.6
• Nitrate (mg/L)	1.95 – 5.85	3.86	0.58 – 2.51	1.25	0.37 – 1.28	0.47	0.77 – 1.96	1.36
• Nitrite (mg/L)	0.1 – 0.3	0.2	bdl	bdl	bdl	bdl	bdl	bdl
• Phosphate (mg/L)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
• Sulfate (mg/L)	3.33 – 6.86	6.19	0.32 – 1.28	0.75	0.43 – 12.9	2.18	1.42 – 2.47	1.94
Trace Metals								
• Copper (µg/L)	12.8 – 22.7	17.3	1.78 – 13.2	4.12	2.30 – 5.20	3.19	5.21 – 8.95	7.08
• Cadmium (µg/L)	0.06 – 0.25	0.19	bdl – 1.52	bdl	bdl – 0.14	bdl	bdl – 0.08	NA
• Nickel (µg/L)	0.76 – 1.46	1.35	bdl – 9.58	0.95	0.12 – 4.32	1.10	1.15 – 4.95	3.05
• Lead (µg/L)	0.10 – 0.64	0.30	bdl – 84.3	bdl	bdl – 1.8	0.22	bdl – 0.42	NA
• Zinc (µg/L)	43.8 – 193	60	10.6 – 45.4	31.7	12.0 – 70.7	23.9	28.7 – 63.5	46.1

Table 4.2: Summary of total constituent concentrations in composite stormwater samples

SITES	I-5		DIXON		WEMME		BEND	
NUMBER OF SAMPLES	5		8		7		2	
PARAMETER (UNITS)	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN	RANGE	MEDIAN
Major Cations								
• Calcium (mg/L)	6.66 – 14.1	9.67	1.80 – 3.96	2.98	2.81 – 21.3	11.2	4.40 – 5.44	4.92
• Magnesium (mg/L)	1.26 – 4.14	1.87	0.38 – 1.14	0.55	0.76 – 106	15.8	5.97 – 14.5	10.2
• Sodium (mg/L)	1.56 – 5.88	2.17	0.66 – 2.83	1.10	0.55 – 8.90	1.52	1.18 – 1.49	1.34
• Potassium (mg/L)	1.52 – 3.79	1.59	0.30 – 0.89	0.55	0.12 – 0.51	0.26	0.51 – 0.77	0.64
• Iron (mg/L)	0.53 – 1.68	0.87	bdl – 1.85	0.54	0.52 – 1.77	0.77	0.44 – 1.69	1.07
Trace Metals								
• Copper (µg/L)	36.8 – 60.9	40.9	4.74 – 26.2	9.91	2.09 – 21.9	9.08	21.8 – 25.8	23.8
• Cadmium (µg/L)	0.37 – 0.74	0.68	bdl – 1.75	bdl	bdl – 0.16	bdl	bdl – 0.12	NA
• Nickel (µg/L)	1.91 – 3.92	2.84	bdl – 10.7	2.10	0.51 – 7.30	1.30	8.40 – 8.50	8.45
• Lead (µg/L)	11.0 – 31.3	15.8	bdl – 101	6.86	2.01 – 25.5	10.4	8.52 – 27.6	18.0
• Zinc (µg/L)	106 – 219	162	26.1 – 189	62.7	31.2 – 138	58.6	148 – 150	149

The Fisher’s LSD simultaneous comparison procedure was used to analyze the differing copper concentrations in the composite samples at individual 95% confidence intervals. Figure 4.1 displays $\text{Cu}^{2+}_{\text{diss}}$ concentrations as a function of site. The I-5 samples consistently contain more $\text{Cu}^{2+}_{\text{diss}}$ than composite samples from other sites. Indeed, all differences in $\text{Cu}^{2+}_{\text{diss}}$ concentrations between I-5 and other sites were significant ($p < 0.05$). The median concentration of $\text{Cu}^{2+}_{\text{diss}}$ in I-5 composites was: 3.78 times higher than Dixon Outfall composites, with a 95% confidence interval (CI) of 2.18-6.58 times the amount. Median $\text{Cu}^{2+}_{\text{diss}}$ concentrations at I-5 were also 5.33 times higher than Wemme composites (3.03-9.38, 95% CI), and 2.40 times higher than Bend composites (1.07-5.40, 95% CI). Additionally, Bend composites showed a median of 2.2 times more $\text{Cu}^{2+}_{\text{diss}}$ than Wemme samples (1.02-4.82, 95% CI). All other comparisons were not significant.

Figure 4.2 shows that somewhat similar results were found in terms of DOC at the different sites. The median concentration of DOC at the I-5 site averaged 1.99 times higher than the median Dixon Outfall concentration (1.15-3.44, 95% CI) and 2.92 times higher than the median Wemme concentration (1.67-5.13, 95% CI). DOC in stormwater can be derived from both natural biologic material and anthropogenic materials (i.e. petroleum based products). All other comparisons of DOC concentrations by site were not significant. The limited number of samples from the Bend site likely plays a role in the inability to determine any significant differences in DOC concentration with other sites.

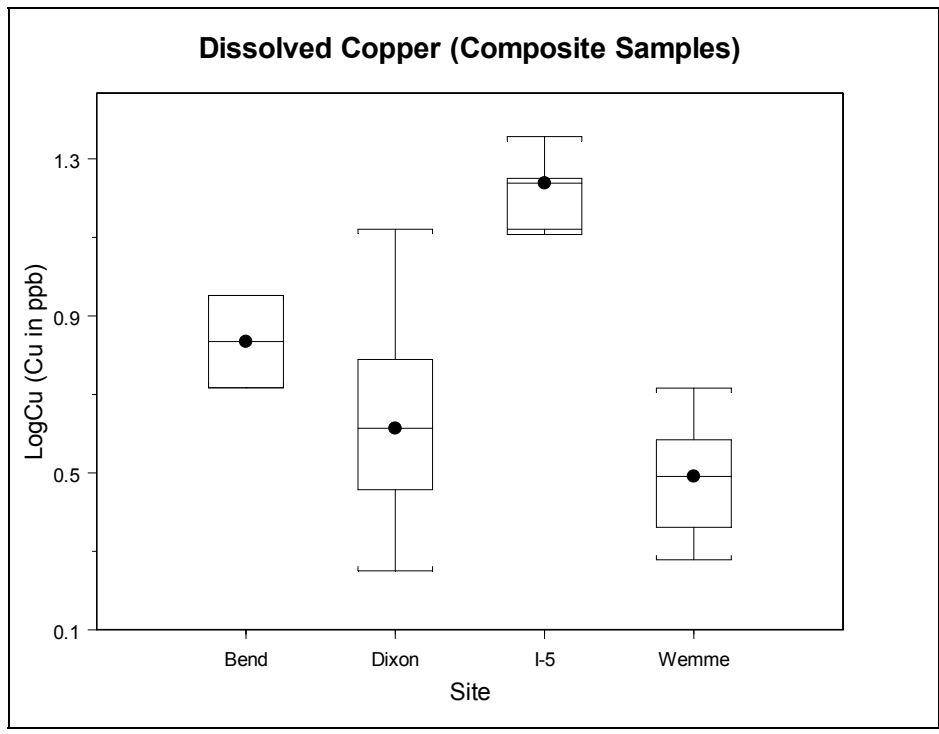


Figure 4.1: Summary of dissolved copper concentrations in composite samples collected at the four sampling sites.

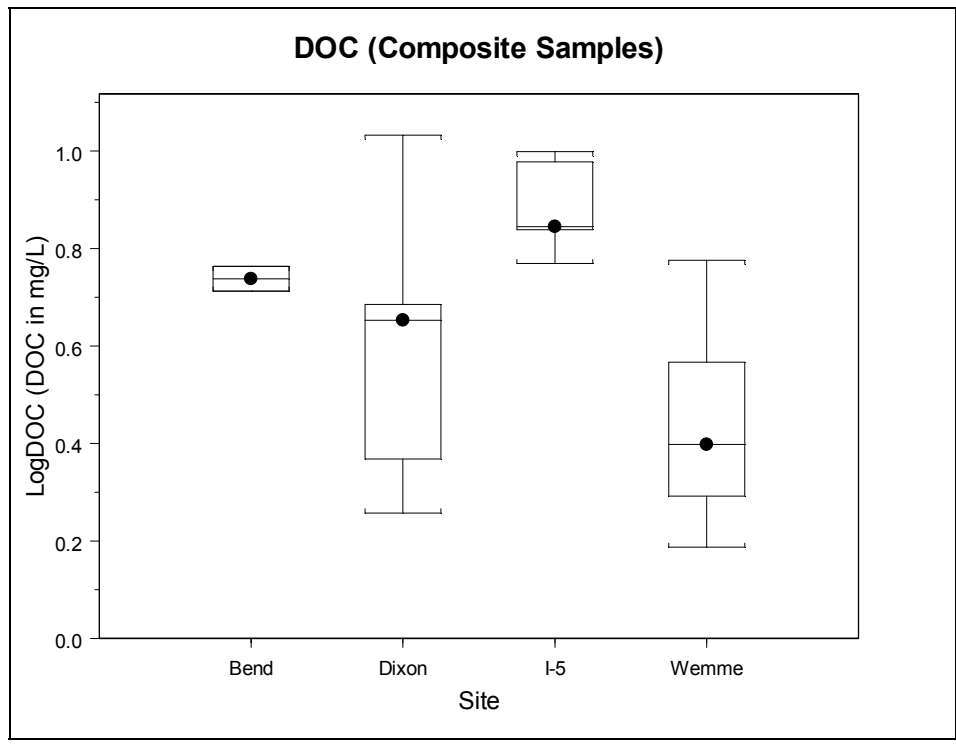


Figure 4.2: Summary of dissolved organic carbon concentrations in composite samples collected at the four sampling sites

Figure 4.3 shows the results for $\text{Cu}^{2+}_{\text{tot}}$ across the four sites. Similar trends were seen with $\text{Cu}^{2+}_{\text{tot}}$ as were witnessed with both $\text{Cu}^{2+}_{\text{diss}}$ and DOC. The median concentration of $\text{Cu}^{2+}_{\text{tot}}$ at I-5 was 4.62 times higher than Dixon Outfall composites (2.26-9.46, 95% CI) and 5.36 times higher than Wemme composites (2.57-11.22, 95% CI). Bend composites showed a median $\text{Cu}^{2+}_{\text{tot}}$ concentration 2.82 times higher than Wemme composites (1.03-7.71, 95% CI). All other comparisons were not significant

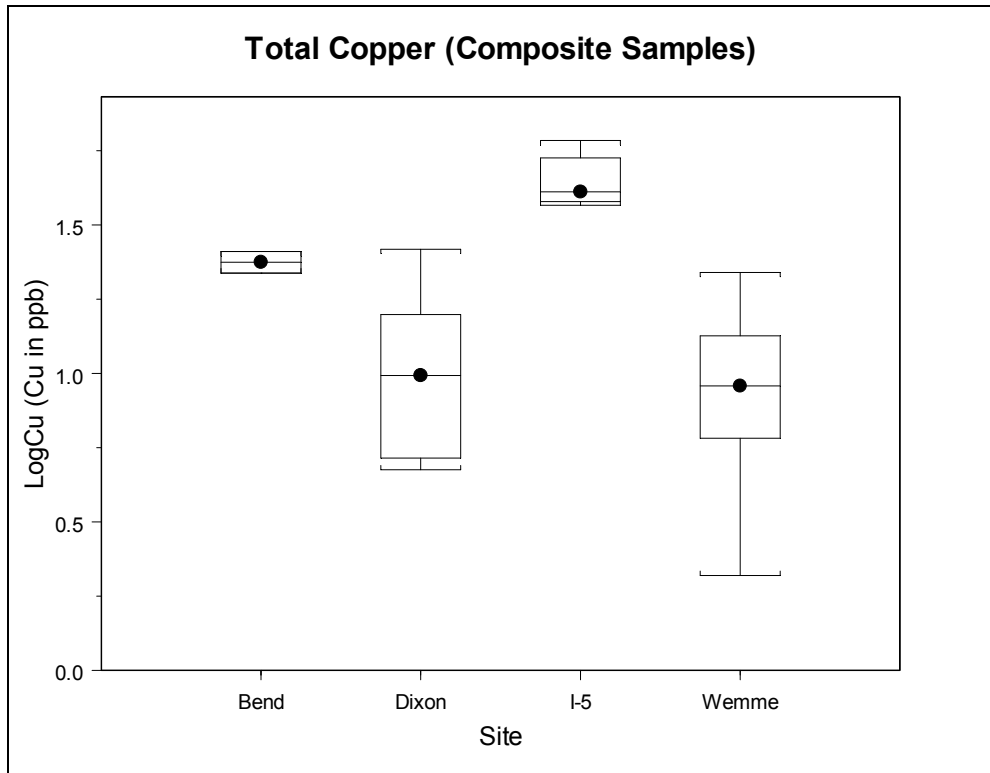


Figure 4.3: Summary of total copper concentrations in composite samples collected at the four sampling sites

The higher concentrations of copper (both total and dissolved) at the I-5 site compared to the others could be due to a variety of factors. Possibly most important among these factors is AADT (since the primary source of copper on highways is brake pads) and urban site association. Using the roadway classification of Kayhanian, et al. (2003) based on AADT levels, only the I-5 site would be classified as urban (specifically medium-high urban) with an AADT of 130,000. All other sites would be classified as non-urban, with AADT levels below 30,000. MLR modeling of $\text{Cu}^{2+}_{\text{diss}}$ as a function of both the I-5 site and AADT showed that only one of these variables is necessary in the model, as they are not simultaneously significant.

In an attempt to focus on the effect of AADT independently from urban association, the composite samples from just the Dixon, Wemme, and Bend sites were examined. The $\text{Cu}^{2+}_{\text{diss}}$ measurements plotted as a function of AADT from all sites and from only the non-urban sites are displayed in Figure 4.4 and Figure 4.5, respectively. The MLR model of the non-urban sites shows insufficient evidence to establish an association between AADT and $\text{Cu}^{2+}_{\text{diss}}$ ($p > 0.05$, two

sided t-test). From this study's dataset, it is only possible to establish that the I-5 site shows higher copper concentrations. The individual effects of AADT and urban site association cannot be conclusively determined with the data presented here.

The lack of a good correlation between traffic and copper concentrations is not surprising, given the differing conclusions reached by previous researchers. Previous research by Kayhanian, et al. (2003) showed that oil & grease was the only runoff pollutant (including copper) to have a strong correlation with AADT. Driscoll, et al. (1990) demonstrated a weak, positive, correlation between AADT and copper with a low R^2 of 0.139. Though significant differences in pollutant concentrations have been demonstrated between sites deemed urban and non-urban, based on AADT, there has been little research to suggest any continuous relationship between pollutant concentrations and traffic density. While the present study also supports that conclusion, the Driscoll and Kayhanian studies collected many more samples at sites with varying AADT levels and therefore reached their conclusions with greater certainty.

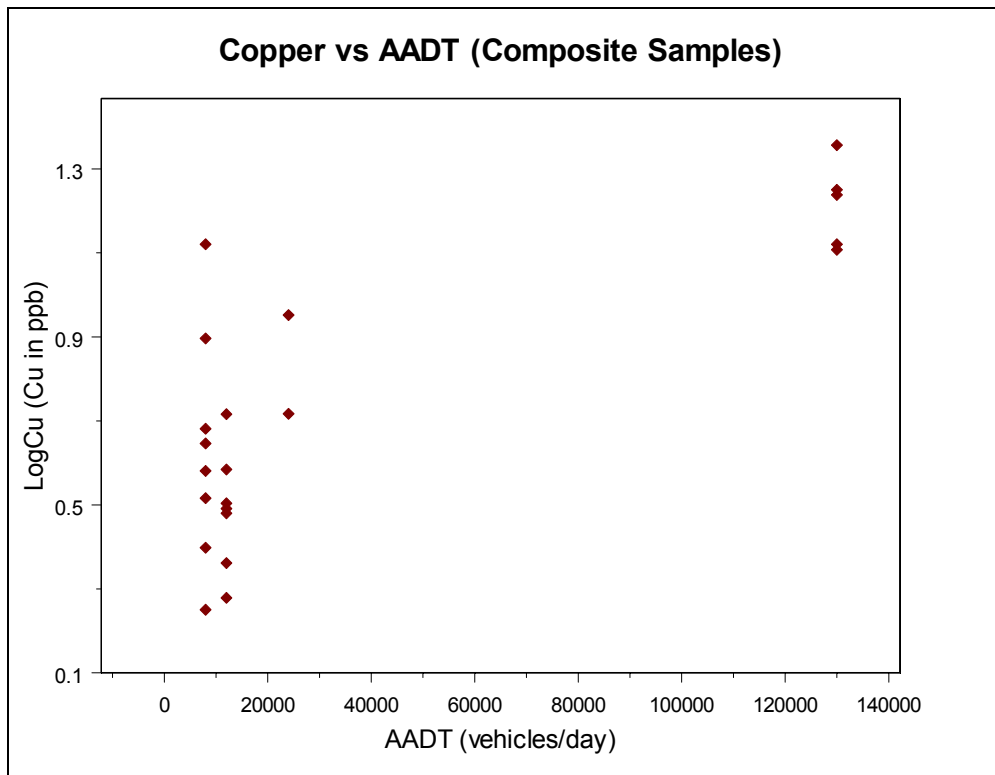


Figure 4.4: Relationship between dissolved copper concentrations in composite samples and annual average daily traffic for all four sampling sites

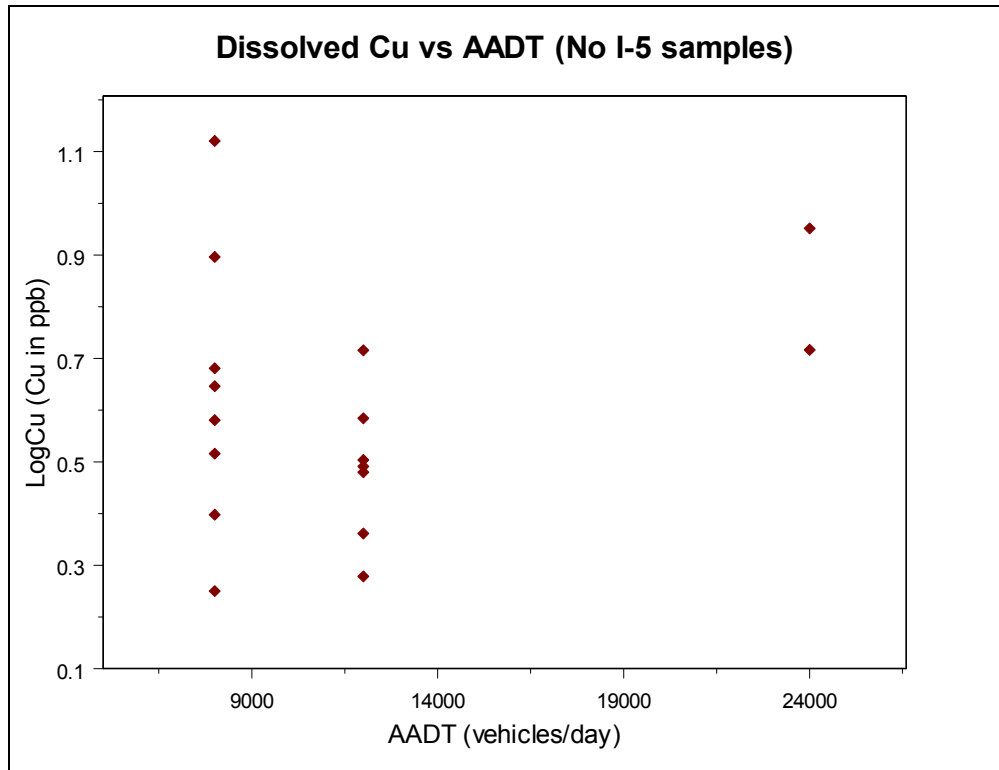


Figure 4.5: Relationship between dissolved copper concentrations in composite samples and annual average daily traffic for the three non-urban sites

4.1.2 The First Flush Effect

Figure 4.6 and Figure 4.7 display the first flush effect for $\text{Cu}^{2+}_{\text{diss}}$ and DOC (respectively) at Dixon Outfall. Both $\text{Cu}^{2+}_{\text{diss}}$ and DOC showed significantly higher concentrations in first flush samples than in composite samples ($p < 0.05$, two sided t-test). On average, first flush samples showed 4.01 times the concentration of $\text{Cu}^{2+}_{\text{diss}}$ found in composite samples (2.20-7.32, 95% CI). In terms of DOC, first flush samples showed an average of 4.75 times the amount found in composite samples (2.83-7.96, 95% CI). The similar correlations of $\text{Cu}^{2+}_{\text{diss}}$ and DOC with the first flush effect suggest a possibility that the $\text{Cu}^{2+}_{\text{diss}}$ present in the stormwater is bound to DOM in the Dixon Outfall samples.

The first flush effect witnessed at the Dixon Outfall site is unsurprising, considering how well-documented the effect is (*Flint and Davis 2007; Han, et al. 2006; Sansalone and Buchberger 1997*). The previously noted studies examined an overall mass first flush – meaning higher copper mass loadings in runoff, while our study only examines the difference in concentrations. Han and coworkers (2006) noted strong first flush behavior for DOC, the most pronounced of a variety of pollutants, including copper. That study also found a strong correlation between the mass first flush ratios of both DOC and $\text{Cu}^{2+}_{\text{tot}}$, which potentially implies a strong correlation between the two parameters. The observation of a first flush for copper suggests that best management practices which control early-storm runoff are likely to decrease the overall effect of copper in receiving waters.

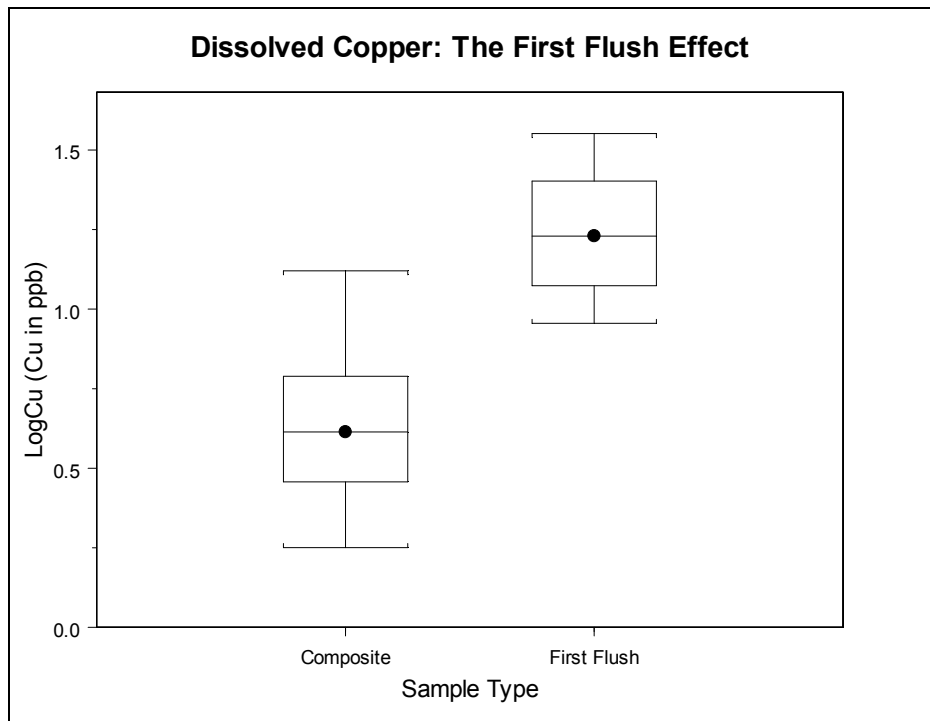


Figure 4.6: Summary of dissolved copper concentrations in composite and first flush samples collected at Dixon Outfall

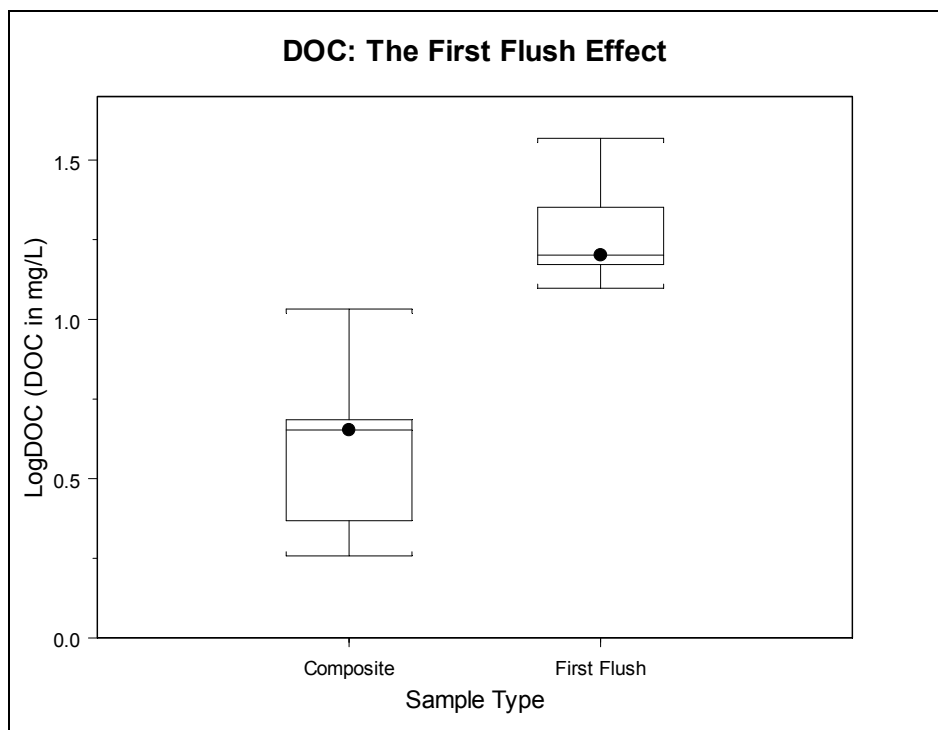


Figure 4.7: Summary of dissolved organic carbon concentrations in composite and first flush samples collected at Dixon Outfall

4.1.3 Relationships with Hydrologic Parameters

The possible effect of hydrologic parameters on copper concentrations could potentially assist in determining what kinds of storms are likely to cause high copper concentrations in receiving waters. To examine the effect of hydrologic variables on $\text{Cu}^{2+}_{\text{diss}}$ in composite samples, a backwards stepwise regression procedure was used. The reduced model contained only the site indicator variables, while the full model contained site indicator variables as well as variables accounting for ADP, total rainfall, and rainfall intensity. Rainfall duration was dropped from the analysis due to its covariation with total rainfall. The graphs displaying the direct relationships between copper and hydrologic variables are shown in Figure 4.8 through Figure 4.11. No apparent relationship arises on inspection of these figures. The MLR analysis confirms the lack of any significant relationship between $\text{Cu}^{2+}_{\text{diss}}$ and these hydrologic parameters after the effect of different sites is accounted for – none of the hydrologic parameters were retained in the final model. However, ADP might be expected to affect first flush concentrations more than composite copper concentrations. This relationship is shown in Figure 4.12 and was examined with the Dixon Outfall samples modeling $\text{Cu}^{2+}_{\text{diss}}$ only as a function of ADP (since all first flush samples are only from Dixon Outfall). No significant statistical association between $\text{Cu}^{2+}_{\text{diss}}$ and ADP was found in first flush samples ($p > 0.05$, two sided t-test).

As noted earlier, the relationship between either total rainfall or rainfall intensity and pollutant EMCs is often weakly negative. Previous studies that revealed pollutant correlations to hydrologic parameters (*Driscoll, et al. 1990; Kayhanian, et al. 2003; USEPA 1983*) examined many more samples than the present study. The lack of any significant correlation found in the present study may be due to a relatively small sample size. This fact may also have contributed to a lack of significant correlation between copper and ADP in both composite and first flush samples. Many factors outside of ADP affect pollutant transport on roadways, so to quantify a direct relationship between concentration and ADP with high confidence would require many samples. Longer ADPs have been shown to have a positive correlation with pollutant EMCs in other studies, though that relationship cannot conclusively be shown here. The samples gathered in this study were primarily from storms in the fall, winter, and spring, and were marked by relatively low ADPs. The infrequency of summer storms (i.e., long ADPs) would have provided data over a much greater range of ADPs. However, their unpredictability (and infrequency) makes sampling these summer storms difficult in terms of practicality.

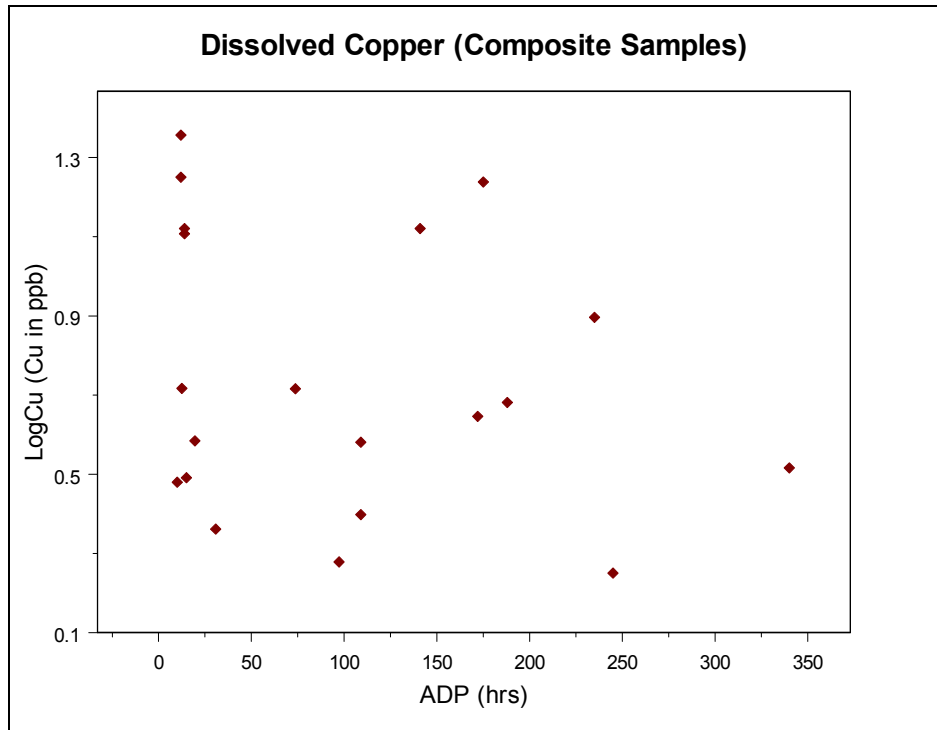


Figure 4.8: Relationship between dissolved copper concentrations in composite samples and antecedent dry period at all four sampling sites

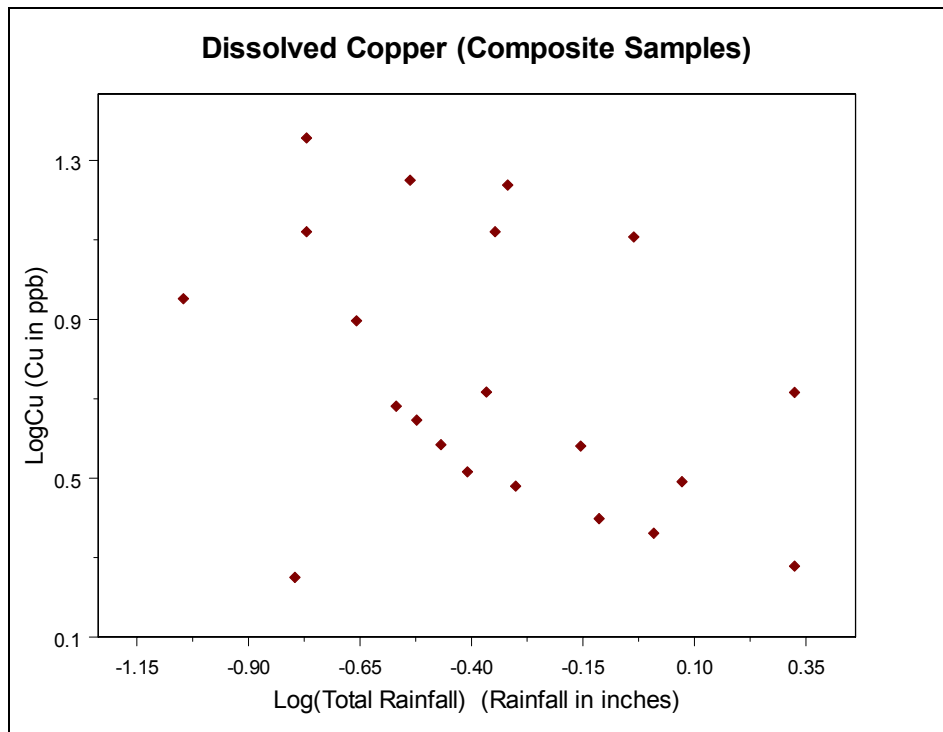


Figure 4.9: Relationship between dissolved copper concentrations in composite samples and total event rainfall at all four sampling sites

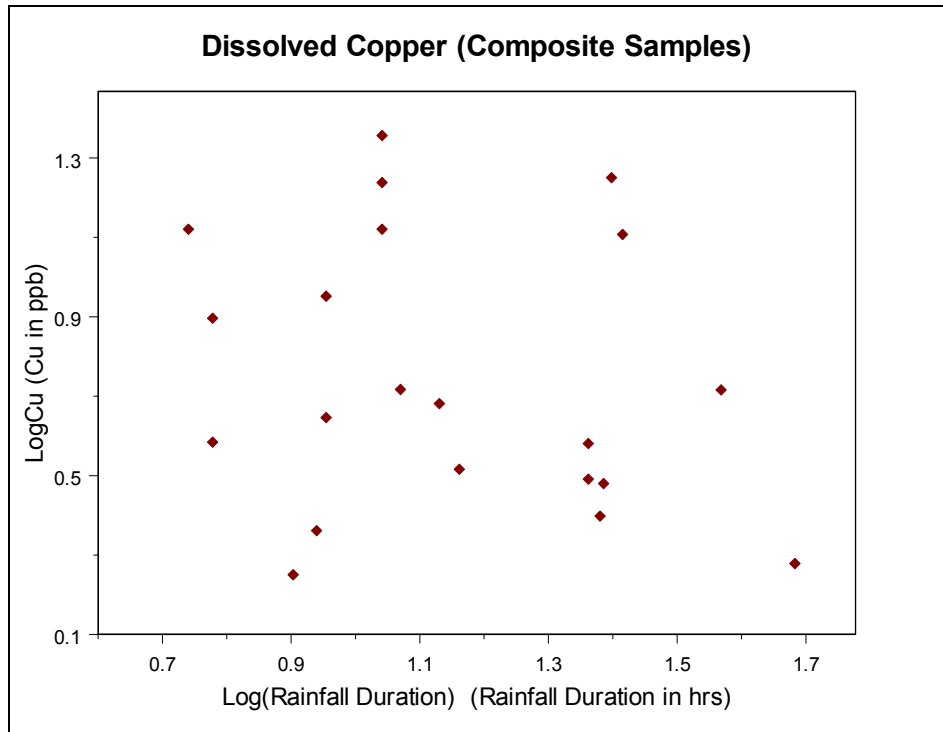


Figure 4.10: Relationship between dissolved copper concentrations in composite samples and rainfall duration at all four sampling sites

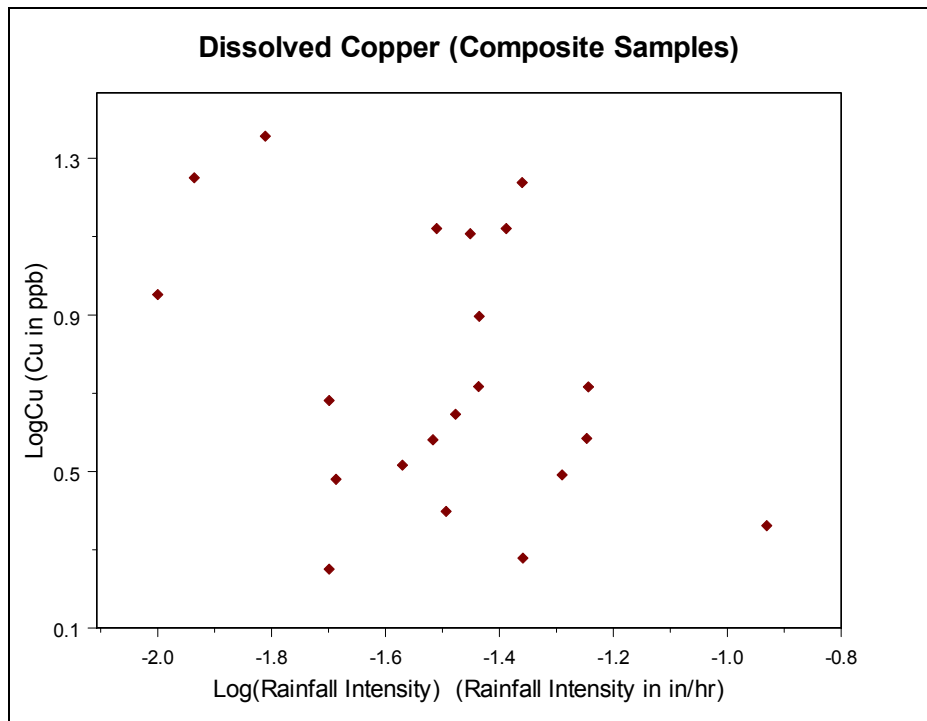


Figure 4.11: Relationship between dissolved copper concentrations in composite samples and rainfall intensity at all four sampling sites

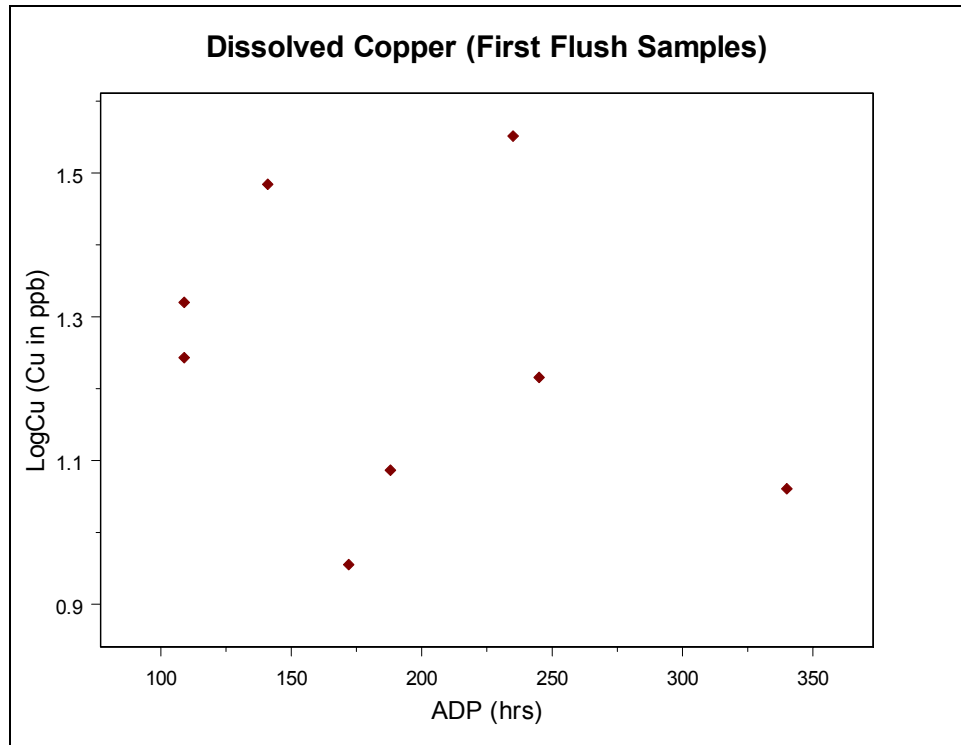


Figure 4.12: Relationship between dissolved copper concentrations in first flush samples and antecedent dry period at Dixon Outfall

4.1.4 Modeling Copper Concentrations with Water Quality Parameters

To examine the effect of water quality parameters on the concentration of $\text{Cu}^{2+}_{\text{diss}}$ in stormwater samples, backwards stepwise regression was employed. This variable selection process differs from the analysis in section 4.1.3 as this process is concerned with using measured concentrations of constituents in the water samples to predict the concentration of copper. The previous analysis looked at parameters which might affect the concentrations of many different constituents, like site association and total rainfall. Since the present MLR analysis did not involve comparing different sites or sample types, but rather the presence of constituents in any water sample, all fully quantified samples were examined. In all, 39 samples of various types (grab, first flush, flow-weighted, composite) and from all four sites were used in the data set. The predictor variables that were examined in the full model were pH, alkalinity, hardness, conductivity, DOC, and TSS. The final model reached in the analysis kept all of the water quality predictor variables with the exception of conductivity. Table 4.3 summarizes the results of this analysis.

Table 4.3: MLR variable selection results for dissolved copper ($\text{Cu}^{2+}_{\text{diss}}$)

Parameter	MLR Relationship w/ $\text{Cu}^{2+}_{\text{diss}}$	p-value
pH	negative	0.0238
Alkalinity	positive	<0.0001
Hardness	negative	0.0321
Conductivity	not significant	not reported
DOC	positive	<0.0001
TSS	positive	0.1168

The most significant variables in predicting $\text{Cu}^{2+}_{\text{diss}}$ were DOC and alkalinity, both having p-values <0.0001 (two-way t-test). Looking at a matrix plot of all the predictor variables (see Appendix A.5), hardness and alkalinity were well-correlated to each other. Therefore, only one of these terms is of great significance to predict $\text{Cu}^{2+}_{\text{diss}}$ in the model (in this case, alkalinity). This association may explain the counterintuitive negative term for hardness in the model in that the hardness term is only accounting for variation not captured by alkalinity. The weak negative association with pH is reasonable, as acidic runoff would be more likely to bring particulate copper into solution. The relatively low p-value may be indicative of the fact that the pH of stormwater samples is approximately neutral and does not vary greatly – so other effects are more pronounced.

The strong positive relationship between DOC and copper has been observed in other studies (*Martinez and McBride 1999; Romkens and Dolfing 1998*) and highlights the ability of large, natural organic matter (NOM) macromolecules to increase the concentration of $\text{Cu}^{2+}_{\text{diss}}$ in solution through complexation. Looking at Figure 4.13, an order of magnitude increase of $\text{Cu}^{2+}_{\text{diss}}$ concentrations at the ppb level are correlated with an order of magnitude increase of DOC at the ppm level. This suggests that while NOM does bind copper, the binding sites are not common moieties on the NOM molecules. Hoffman, et al. (2007) suggested that copper is bound to uncommon binding sites or sites with special conformation within the macromolecule. The Hoffman research concluded that bulk NOM characteristics, such as aromaticity and elemental ratios, are not very important in determining the ability of NOM to bind trace metals. Though relatively few sites are likely able to bind copper within a NOM molecule, NOM is often present in great excess compared to copper.

Graphs showing the DOC- $\text{Cu}^{2+}_{\text{diss}}$ and alkalinity- $\text{Cu}^{2+}_{\text{diss}}$ correlations can be seen in Figure 4.13 and Figure 4.14, respectively. The association of these two parameters with increased copper levels does not necessarily imply causation. The association of $\text{Cu}^{2+}_{\text{diss}}$ with DOC or alkalinity may only demonstrate the presence of many pollutants, including copper, in the runoff samples. However, the simultaneous significance of these two parameters in predicting $\text{Cu}^{2+}_{\text{diss}}$ means they are accounting for distinct effects in the samples. If both of these parameters only accounted for a positive variation with overall increased pollutant concentrations in stormwater (including copper), they would not both have been found to be so significant in the final model. DOC and alkalinity are also more easily quantified than trace metals but may provide some information on the amount of $\text{Cu}^{2+}_{\text{diss}}$ during a runoff event.

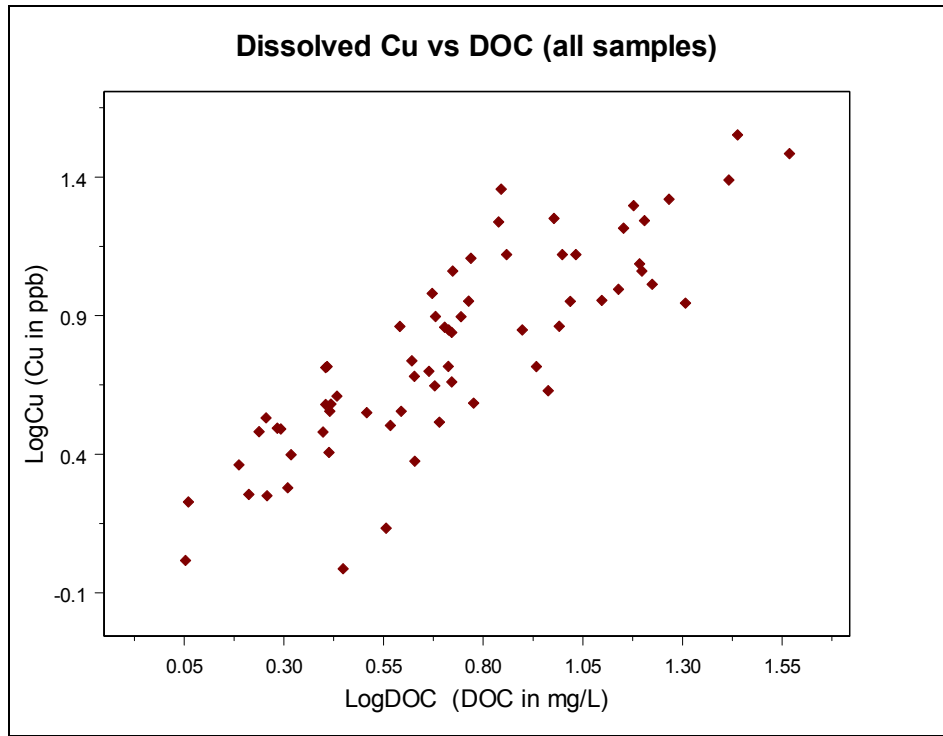


Figure 4.13: Relationship between dissolved copper and dissolved organic carbon in all samples

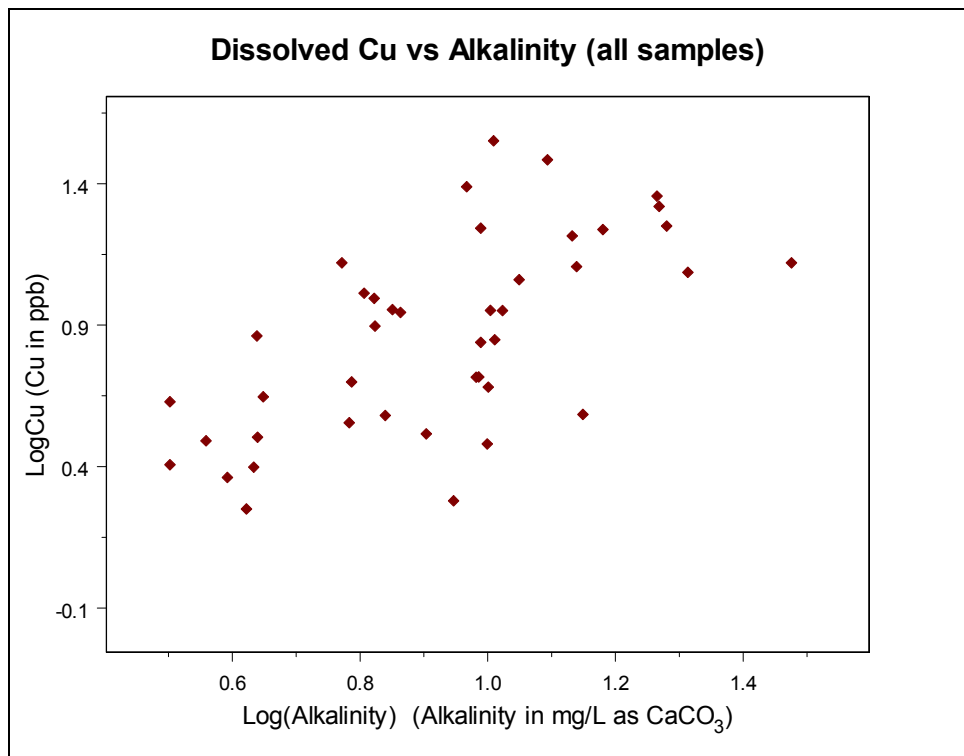


Figure 4.14: Relationship between dissolved copper and alkalinity in all samples

Determining a model for $\text{Cu}^{2+}_{\text{tot}}$ in samples was done in a similar manner to the model-building process for $\text{Cu}^{2+}_{\text{diss}}$. The predictor variables that were examined in the full model were hardness, DOC, and TSS, and the analysis was done on the same 39 samples examined in the $\text{Cu}^{2+}_{\text{diss}}$ model. Table 4.4 below summarizes the results of this analysis.

Table 4.4: MLR variable selection results for total copper ($\text{Cu}^{2+}_{\text{tot}}$)

Parameter	MLR Relationship w/ $\text{Cu}^{2+}_{\text{tot}}$	p-value
Hardness	not significant	not reported
TSS	positive	<0.0001
DOC	positive	<0.0001

The final model showed significant positive associations of $\text{Cu}^{2+}_{\text{tot}}$ with both TSS and DOC ($p < 0.0001$). The direct $\text{Cu}^{2+}_{\text{tot}}$ -TSS and $\text{Cu}^{2+}_{\text{tot}}$ -DOC relationships are shown in Figure 4.15 and Figure 4.16, respectively. The matrix plot for this MLR model showed covariation between hardness and TSS. So again, only one of these terms is necessary in the final model.

Since metals are either deposited on the roadway as TSS or are bound to other particles, TSS is an important parameter in predicting the presence of metals in stormwater samples (*Herngren, et al. 2005*). Although the correlation of TSS with $\text{Cu}^{2+}_{\text{tot}}$ is unsurprising, the direct relationship between $\text{Cu}^{2+}_{\text{tot}}$ and TSS does not appear particularly strong. The absence of TSS as an important variable in the $\text{Cu}^{2+}_{\text{diss}}$ model may indicate that other water quality parameters, primarily DOC and alkalinity, may facilitate the dissolution of copper.

As with $\text{Cu}^{2+}_{\text{diss}}$, DOC is still an important variable in predicting $\text{Cu}^{2+}_{\text{tot}}$ concentrations, likely due to copper's affinity for NOM. The simultaneous significance of both TSS and DOC in this model is reasonable: a) DOC remains an important predictor variable, as it accounts for much of the variation in copper in the dissolved fraction of the samples; and b) TSS becomes an important predictor, as it accounts for any copper which remained adsorbed to solids in the sample. These two fractions are summed in the measurement of the total samples.

Since $\text{Cu}^{2+}_{\text{diss}}$ predictably correlates with $\text{Cu}^{2+}_{\text{tot}}$ (see Figure 4.17), another MLR model was constructed to see if DOC or alkalinity had any effect on $\text{Cu}^{2+}_{\text{diss}}$ concentrations after the concentration of $\text{Cu}^{2+}_{\text{tot}}$ present was accounted for. This model revealed that, after accounting for the effect of $\text{Cu}^{2+}_{\text{tot}}$, DOC was still a significant predictor of $\text{Cu}^{2+}_{\text{diss}}$ ($p < 0.0001$, F-test). Alkalinity showed an insignificant association with $\text{Cu}^{2+}_{\text{diss}}$ after $\text{Cu}^{2+}_{\text{tot}}$ had been accounted for in the model ($p = 0.19$, F-test). These findings suggest that while both alkalinity and DOC are associated with $\text{Cu}^{2+}_{\text{diss}}$, only the relationship with DOC could potentially be causative. The inclusion of alkalinity in the $\text{Cu}^{2+}_{\text{diss}}$ model may only be indicative of the presence of $\text{Cu}^{2+}_{\text{tot}}$. This is a reasonable conclusion – DOM has a strong affinity for copper and is likely to cause particulate copper (part of the $\text{Cu}^{2+}_{\text{tot}}$ measurement) to partition into the dissolved phase.

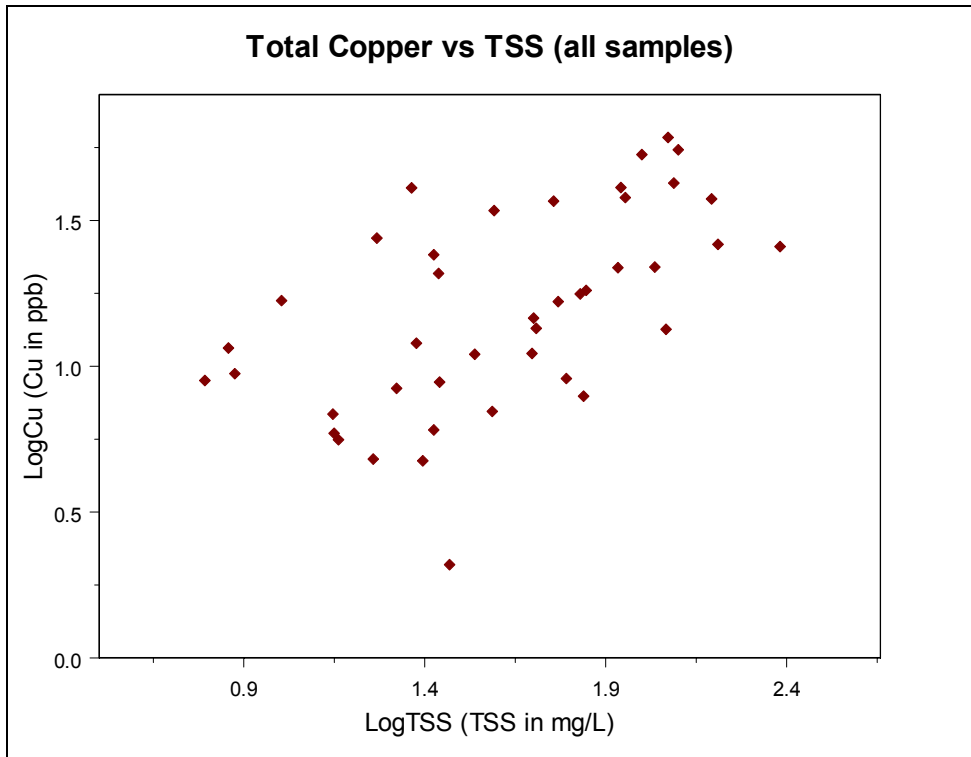


Figure 4.15: Relationship between total copper concentrations and total suspended solids in all samples

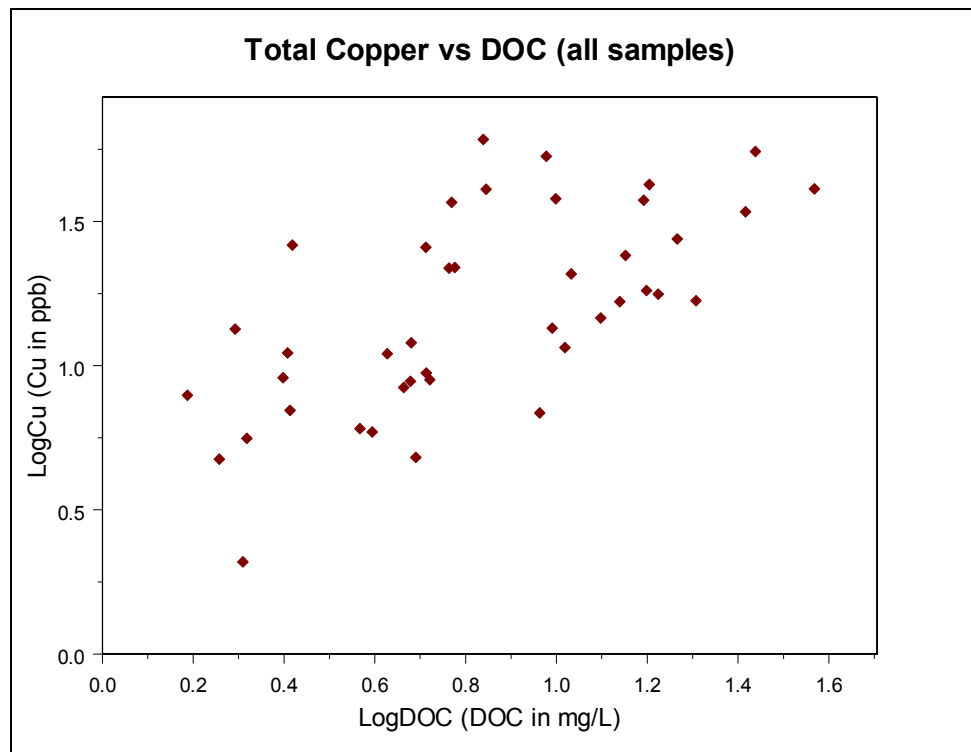


Figure 4.16: Relationship between total copper concentrations and dissolved organic carbon in all samples

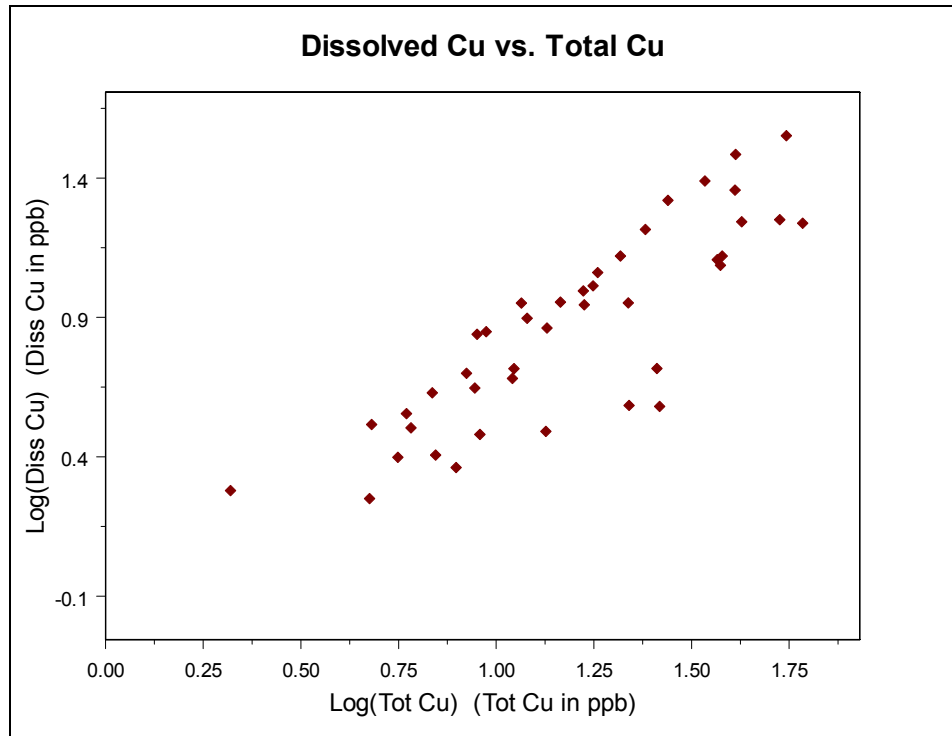


Figure 4.17: Relationship between dissolved and total copper concentrations in all samples

4.1.5 Intra-Storm Variations in Copper Concentration

Flow-weighted samples collected throughout 9 different storms were examined at the Dixon Outfall site. These flow-weighted samples were measured for dissolved trace metals and DOC. An example of the data collected is shown in Figure 4.18, for the 10/13 to 10/14/09 storm at Dixon Outfall. This figure shows higher concentrations of $\text{Cu}^{2+}_{\text{diss}}$ and DOC present in samples analyzed early in a storm as opposed to those collected later in the storm's progression. Furthermore, the drop in concentrations of both copper and DOC after the first flush is precipitous at first, and more gradual as the storm continues. This trend was consistent in other storms as well. This figure also suggests a weak flush occurring subsequent to a pause in the storm. For example, the concentrations of $\text{Cu}^{2+}_{\text{diss}}$ and DOC slightly increased from the 2nd to the 3rd samples from this storm; between these two samples there was a 4-hour break in the storm. This short dry period may have allowed a small amount of pollutant accumulation on the roadway, which resulted in the jump in $\text{Cu}^{2+}_{\text{diss}}$ and DOC concentrations present in the 3rd sample. This plot also agrees with the strong correlation of copper and DOC discussed previously. In all cases, a relative increase or decrease in DOC between two flow-weighted samples has a corresponding increase or decrease in $\text{Cu}^{2+}_{\text{diss}}$.

The intra-storm data was analyzed with simple linear regressions, modeling $\text{Cu}^{2+}_{\text{diss}}$ or DOC concentration as a function of V_i/V_{tot} , or 'normalized cumulative volume.' V_i/V_{tot} is a ratio which represents the cumulative volume of runoff when sample i was taken divided by the total runoff volume produced by the storm. This measure can be applied to all storms and is used here to show the overall progress of a storm. Both $\text{Cu}^{2+}_{\text{diss}}$ and DOC concentrations were found to

significantly decrease over the course of individual storms ($p < 0.05$, two sided t-tests). Graphs of these results are shown in Figure 4.19 and Figure 4.20.

Though used in this simple analysis, V_i/V_{tot} is by no means an accurate predictor of Cu^{2+}_{diss} . The primary weakness of this parameter is that it does not reveal the magnitude of a storm. A sample collected at a given V_i/V_{tot} within a large storm would be expected to have more dilute concentrations of pollutants than another sample with the same V_i/V_{tot} from a small storm. Additionally, there may not be a linear relationship between V_i/V_{tot} and Cu^{2+}_{diss} . The most important result of this analysis is the significant decrease in copper and DOC throughout the course of a storm, which is also apparent in the figures.

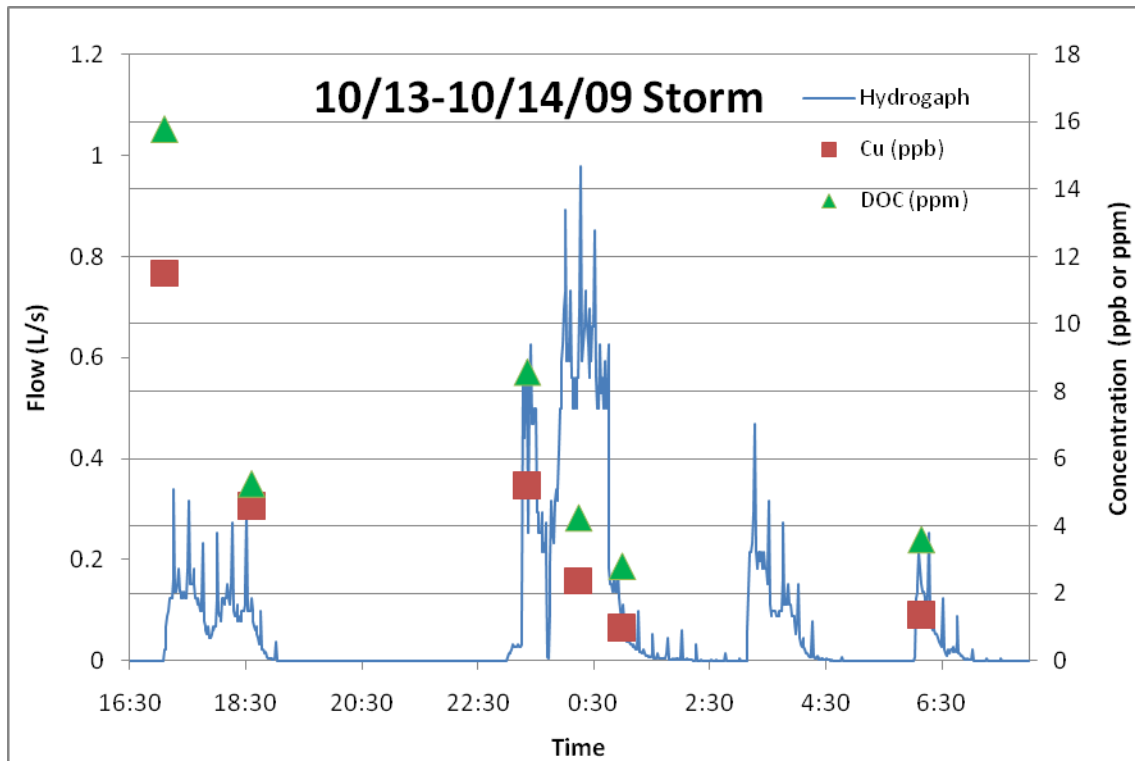


Figure 4.18: Variation of dissolved copper and dissolved organic carbon concentrations over the course of a single storm at the Dixon Outfall site

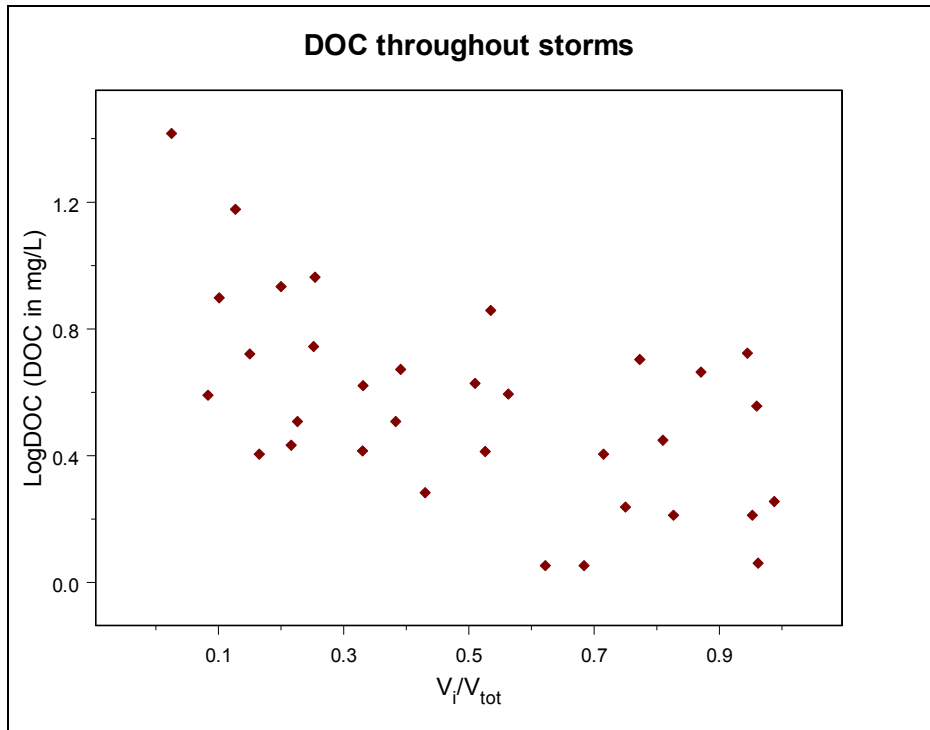


Figure 4.19: Variation of dissolved organic carbon concentrations throughout the course of all storms collected at the Dixon Outfall site. Progress through the storm is represented as the normalized cumulative volume.

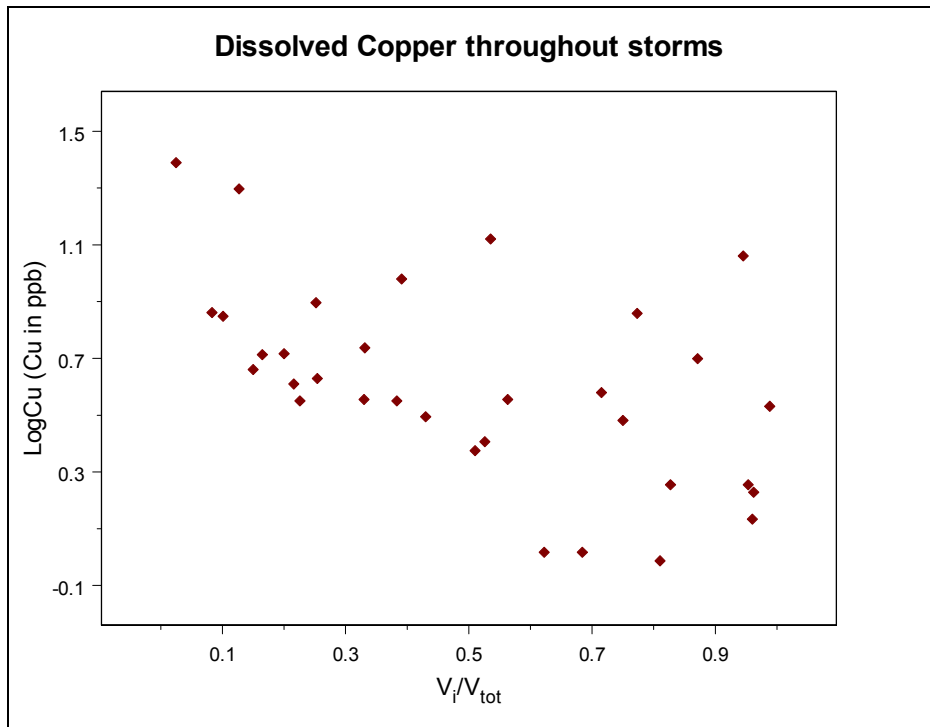


Figure 4.20: Variation of dissolved copper concentrations throughout the course of all storms collected at the Dixon Outfall site. Progress through the storm is represented as the normalized cumulative volume.

4.2 COPPER SPECIATION IN COMPOSITE SAMPLES

This section details the application of the methodology described in Chapter 3 to determine the speciation of copper in 21 composite stormwater samples collected from the Bend, Wemme, I-5, and Dixon Outfall sampling sites. First, the competition strength of the added ligand (SA) was determined; this consisted of determining the value of α_{CuSA_x} as described previously. α_{CuSA_x} values determined in this study are presented and contrasted with previously reported values for natural waters. Second, the analytical procedures and data analysis procedures used for determining copper speciation are discussed using one stormwater sample as an example. Speciation results are discussed on a site-by-site and a parameter-by-parameter basis. Third, the correlations of free ionic copper and organic ligand concentrations with aggregate water quality parameters are examined. Finally, free ionic copper concentrations determined in this study are compared to those predicted using three different Visual MINTEQ DOM models.

4.2.1 Determination of α_{CuSA_x}

As described in Chapter 3, the binding strength of the added ligand is characterized through the side-reaction constant α_{CuSA_x} ; values of the constant determined in this study are tabulated in Table 4.5. Alpha values decreased with increasing calcium concentration (see Figure 4.21), suggesting that calcium was competing with copper for SA binding sites.

Table 4.5: Log alpha values for salicylaldoxime (all values at $I = 0.05M$, pH 6.80)

[SA]	[Ca]	Hardness	$\log \alpha_{CuSA_x}$ ^a
μM	mg/L	mg/L CaCO ₃	
2	1	2.5	-- ^b
	10	25	4.22±0.06
	50	125	3.66±0.10
10	1	2.5	5.81±0.11
	10	25	4.37±0.09
	50	125	3.79±0.14

Notes:

(a) Alpha values were reported with one standard deviation.

(b) Alpha value for 2 μM SA at 1ppm Ca was omitted due to noisy instrument response/plots and low instrument response in the blank.

These results confirm earlier finding by Monticelli, et al. (2004) and Campos and van den Berg (1994). Differences between the calculated alpha values for this study and previous studies can be attributed to pH and ionic strength. Alpha values reported in this study are greater than those reported by Monticelli, et al. (2004). The differences between the results can be attributed to ionic strength differences. Ionic strength increases lead to increases in instrument response and stability constants, resulting in greater alpha values. The instrument response effects of ionic strength are reduced (though not eliminated) due to the lower pH used in this study. The decreased pH used in this study led to decreased HSA⁻ concentrations and a corresponding decrease in α_{CuSA_x} .

Differences between the alpha values determined at SA concentrations of 2 and 10 μM in this study were not as great as expected. Previous studies reported alpha values calculated at different SA concentrations as more distinct. The reasons for this discrepancy are unknown.

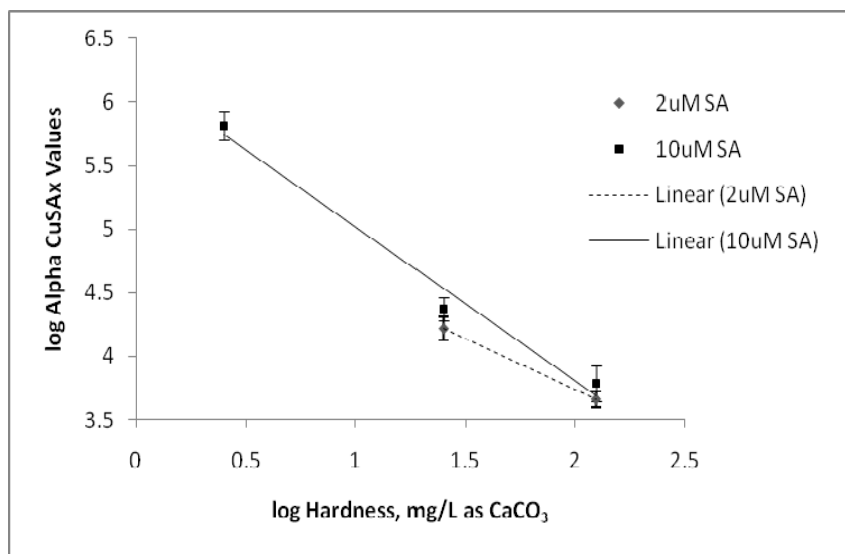


Figure 4.21: Variation of α_{CuSAx} with hardness

4.2.2 Method Verification

Preliminary speciation experiments were performed on Willamette River water in order to verify the method. Results from these experiments were very positive, producing copper titration curves (see below) with sensitivity (0.8 nA/nM Cu) and appearance close to those reported by Campos and van den Berg (0.86 nA/nM Cu). To test the effects of surfactants on the method, a range of Triton X concentrations were added to Willamette samples. Interpreting the titration with the internal slope (sensitivity), ligand information was recovered up to 3mg Triton X/L (but not at 6 mg/L). Therefore, speciation results from samples containing high concentrations of surfactants will likely not be accurate.

4.2.3 Analytical Procedures and Data Analysis

For the purpose of illustration, the analytical procedure and analysis of the data from one representative composite sample collected at the Wemme site (3/24/09) is discussed in detail to demonstrate the procedure that was followed and the results that were obtained. These same procedures were utilized for all stormwater samples. Figure 4.22 is an example of a voltammogram (stripping potential vs. instrument response) obtained from one of the many 10 mL aliquots analyzed from the Wemme site sample. Curves like these were produced as Cu^{2+} was reduced to Cu^0 at the mercury electrode after adsorbing onto the drop as CuSA_2 . This specific figure represents a 100 nM Cu addition during a titration in which the added copper concentration was varied from 0 to 200 nM. Copper peaks in this study were typically centered

at -0.14 volts (-0.12 to -0.18 volts). This is in contrast to the work of Campos and van den Berg, where peaks were centered at approximately -0.36 volts. Lower copper reduction potentials compared to the Campos and van den Berg study are due to pH differences (*Campos and van den Berg 1994; Wang 1985*).

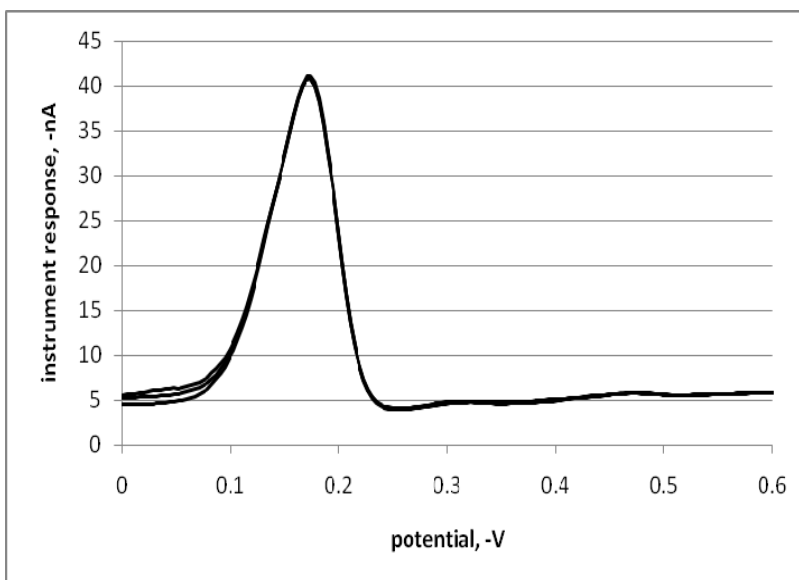


Figure 4.22: Triplicate voltammograms of the Wemme 3/24/09 composite sample containing $2 \mu\text{M}$ SA and 100 nM of added copper

4.2.3.1 Copper Titrations

Figure 4.23 is the titration curve produced for the Wemme sample with $2 \mu\text{M}$ of SA. As copper is added to the sample, the concentration of the electroactive complex CuSA_2 increases, leading to a rise in measured peak current (i_p). Eventually, with continuing copper additions, the sites on the natural organics in the sample become saturated with copper. At this point, the titration curve becomes linear due to the fact that additional copper is bound solely by SA; the slope of this region is equal to the sample sensitivity (S). As shown previously, the sensitivity is used to determine $[\text{CuSA}_x]$ using Equation (3-6). As described in Chapter 3, using this internal slope can correct for signal suppression due to surfactants (*Kogut and Voelker 2001*). Figure 4.23 illustrates the sensitivity determination for the Wemme sample.

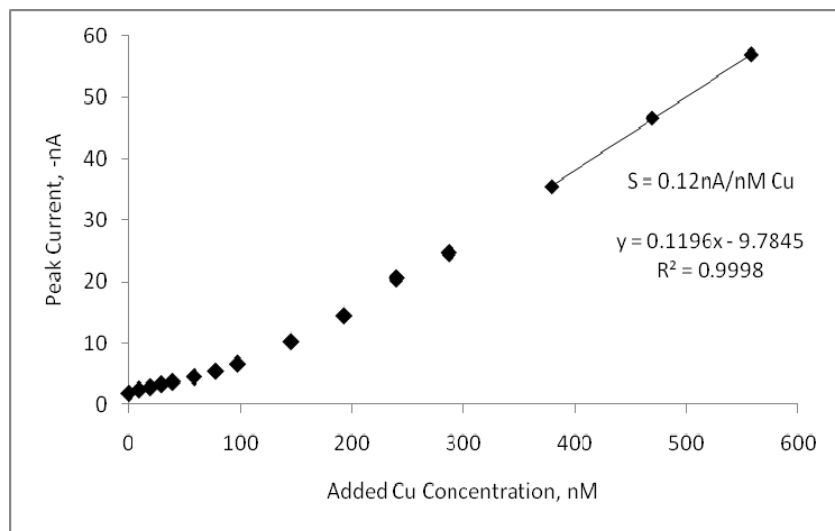


Figure 4.23: Copper titration of Wemme composite sample from 3/24/09 containing 2 μM SA

4.2.3.2 Determination of Natural Ligand Concentration and Strength

All speciation data were fit to Equation (3-9) following the Langmuir non-linear curve fitting method described in Section 3.2.10.6. Figure 4.24 illustrates how the ligand concentration and stability constant information is obtained from this procedure. The total concentration of ligands (i.e., sites), $[L_T]$, calculated for the Wemme 3/24/09 sample was 161.5 nM; the conditional stability constant for the Cu-Ligand complex, K'_{CuL} , was $10^{10.92}$.

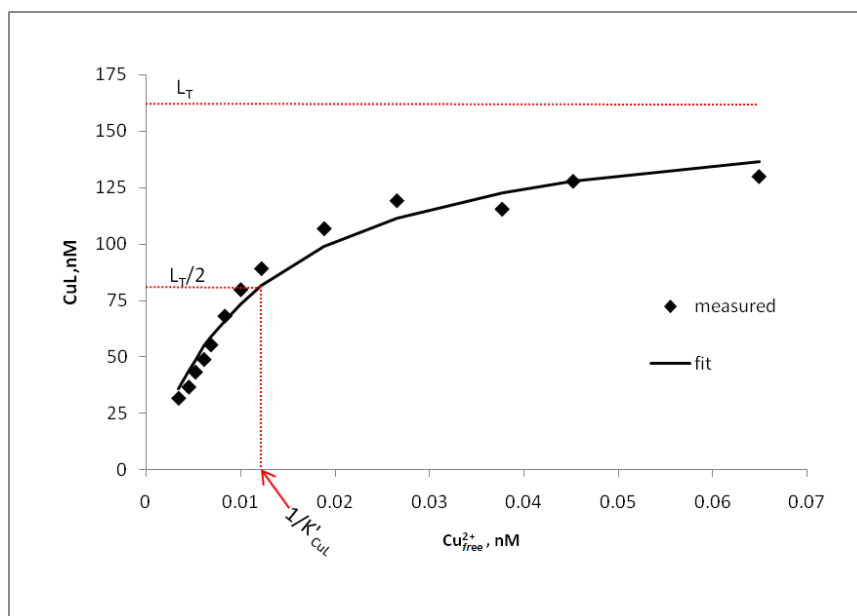


Figure 4.24: Non-linear least squares fit of the titration data from the Wemme 3/24/09 composite sample containing 2 μM SA to a Langmuir-type expression, describing complexation of copper with the organic ligands in the sample

4.2.3.3 Detection Windows

The competitive strength of the added ligand (α_{CuSAx}) can be adjusted through the variation of the added SA concentration. Ligands of different strengths can be selectively outcompeted by varying the competition strength of the added ligand (thereby varying the concentration of SA). This phenomenon can be utilized to obtain ‘snap shots’ of different natural ligand populations and their respective stability constants. Bruland, et al. (2000) have termed these analyses ‘detection windows.’ Ligand information within the same window can be compared readily, whereas it is impossible to quantitatively compare that same information across windows (Bruland, et al. 2000; Buck and Bruland 2005). Two detection windows were used in this study, 2 and 10 μM SA, to provide information on strong and weak ligands in the system. Figure 4.25 is a comparison of the titration curves obtained using the two detection windows for the Dixon Outfall 2/06/09 composite sample.

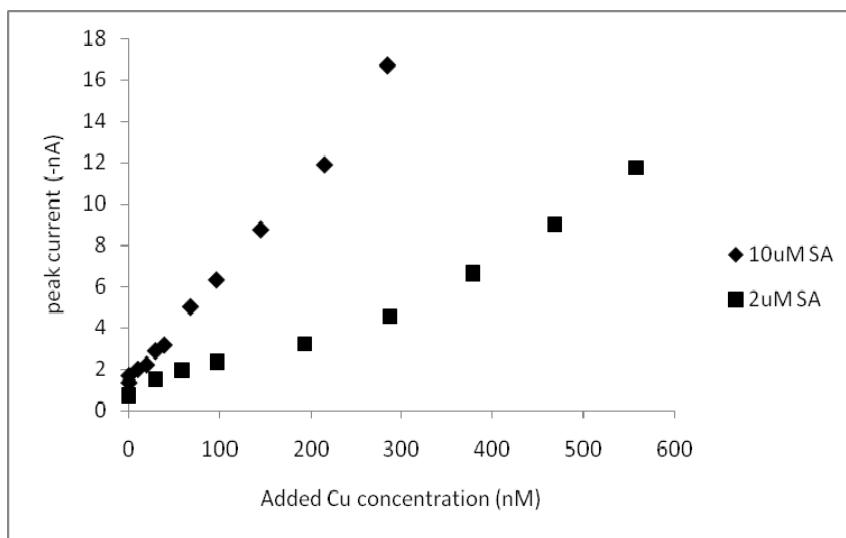


Figure 4.25: Copper titrations of the Dixon 2/06/09 composite sample at two detection windows (2 and 10 μM SA)

Applying the Langmuir non-linear curve fitting method to both titrations for the 2/06/09 Dixon composite sample leads to two separate ligand concentrations and stability constants. The lower (2 μM SA) detection window reveals a ligand concentration of 335 nM and a stability constant of $10^{11.26}$. The higher (10 μM SA) window reveals a lower ligand concentration, 68.4 nM, and a higher stability constant, $10^{12.80}$. Comparison between each detection window for the five samples tested with both SA levels reveals that ligand concentrations decrease and stability constants increase with the shift from 2 to 10 μM SA. This behavior is reflected in previous studies in natural waters (Bruland, et al. 2000, Buck and Bruland 2005). Figure 4.26 and Figure 4.27 present non-linear least squares fits of the titration data from the Dixon Outfall 2/06/09 composite sample to Equation (3-9).

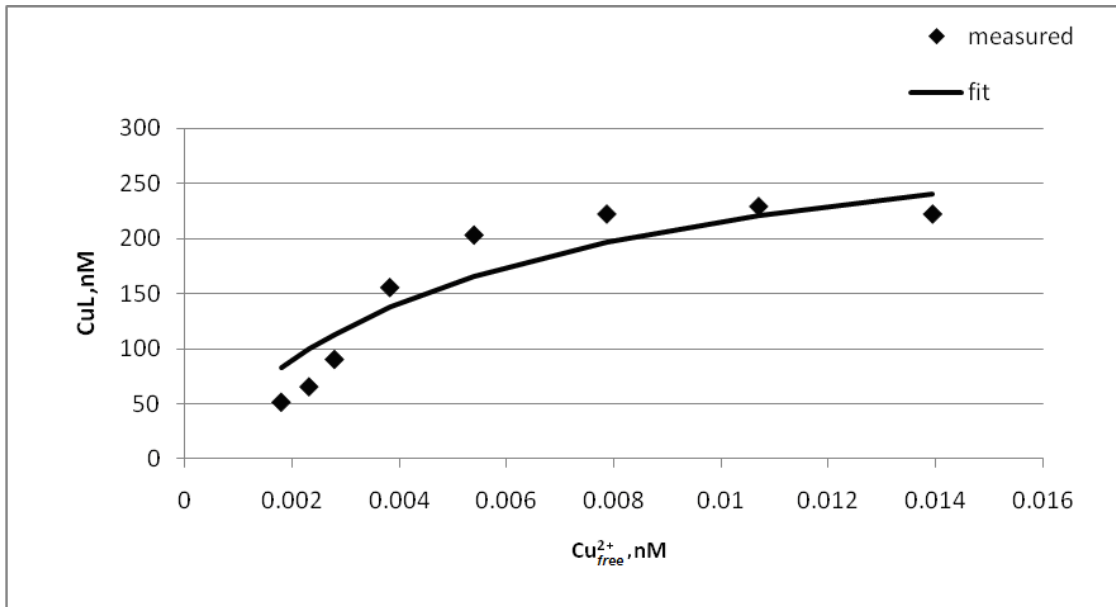


Figure 4.26: Non-linear least squares fit of copper titration data from the Dixon Outfall 2/06/09 composite sample containing 2 μM SA

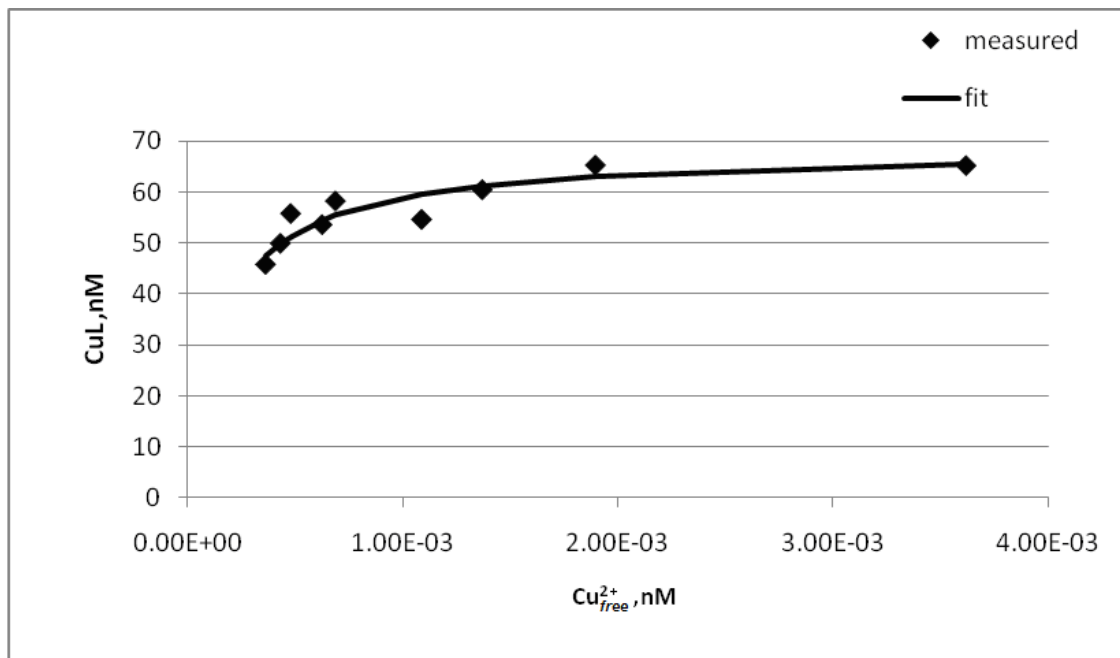


Figure 4.27: Non-linear least squares fit of copper titration data from the Dixon Outfall 2/06/09 composite sample containing 10 μM SA

The high detection window for this study (10 μM SA) led to titration curves that became linear at low added copper concentrations. This behavior is due to the high $\text{Cu}^{2+}_{\text{diss}}$ concentrations relative to the number of available natural ligand sites in some stormwater samples. The ligand

sites in samples with high Cu^{2+}_{diss} concentration were (mostly) filled with copper before the titration started, essentially truncating the titration curves and eliminating the curved portion. In these situations, the resulting Langmuir curve is truncated and little information about stability constants is provided at low Cu^{2+}_{free} concentrations (see Figure 4.27 for an example). Other (erroneous) fitted data sets had decreasing trends (negative slopes) with increasing Cu^{2+}_{free} concentration and/or negative CuL values for the entire range of Cu^{2+}_{free} concentrations. These results are discussed below in the Wemme site overview.

4.2.4 Copper Speciation Results

Total ligand concentrations and conditional stability constants determined for all composite samples are listed in Table 4.6. Water quality parameters (excluding pH and temperature) known to affect either free ionic copper concentrations or copper toxicity are supplied alongside the speciation results. $[Cu^{2+}_{diss}]$ represents the total dissolved copper concentration; $[L_T]$ represents the natural organic ligand concentrations; K'_{CuL} is the stability constant associated with those ligands; $[Cu^{2+}_{free}]$ represents uncomplexed, or free ionic copper; and ‘Cu Complexation’ is the percentage of Cu^{2+}_{diss} that was complexed by organic ligands in the sample. Cu^{2+}_{free} concentrations were calculated using Equation (3-10), but where samples had $[L_T] < [Cu^{2+}_{diss}]$ then a ‘worst case’ scenario was assumed and Cu^{2+}_{free} concentrations were approximated as $[Cu^{2+}_{diss}] - [L_T]$. Stormwater samples that fell into this category were re-tested at 2 μ M SA when sample volume allowed. Lowering the detection window usually resulted in a more representative picture of the organic ligands. In most of these cases, the lower detection window revealed the presence of a population of weaker ligands, implying that the ligands in these samples were weaker and easily outcompeted by 10 μ M of SA.

Differences between ligand concentrations and stability constants were significant for the two detection windows at 2 μ M and 10 μ M SA. The mean ligand concentration determined in the 10 μ M SA detection window was 187.2 nM less than the mean ligand concentration determined with 2 μ M SA (–325.2 to –49.1 nM, 95% CI). The mean (log) conditional stability constant value determined in the 10 μ M SA window was 1.1 log units more than the mean (log) stability constant determined with 2 μ M SA (0.6 to 1.7 log units, 95% CI). The differences in stability constants and ligand concentrations between detection windows is corroborated by Buck and Bruland (2005). It is important to recognize that this analytical procedure assumes that there is a single population of ligands with a defined binding strength. In reality, the DOM in the stormwater samples is a heterogeneous mixture of organic molecules that have different binding strengths. This “fitting” of the data to a single population of ligands is the reason for the differences in the ligand concentrations and binding strengths determined at the different detection windows. For this reason, only ligand information (total concentration and stability constant) from a single detection window can be compared (Buck and Bruland 2005). Calculated Cu^{2+}_{free} concentrations are independent of the detection window; thus, calculated Cu^{2+}_{free} concentrations determined at the 2 μ M and 10 μ M SA detection windows can be compared.

Table 4.6: Ligand characteristics, free ionic copper concentrations and related water quality parameters for composite samples collected at all sites

Site	Storm	SA μM	[Cu ²⁺ _{diss}]		DOC mg/L	Hardness mg/L as CaCO ₃	Alkalinity mg/L as CaCO ₃	[L _T] nM	log K' _{CuL}	log [Cu ²⁺ _{free}] M	Cu Complexation %
			μg/L	nM							
Bend	12-29-08	10	5.21	82.00	5.16	27.30	9.68	173.58	11.65	-11.69	99.99
	03-16-09	10	8.95	140.86	5.80	72.84 ^a	10.1	114.15	11.89	-7.57 ^c	81.04
	03-16-09	2	8.95	140.86	5.80	72.84 ^a	10.1	432.73	10.54	-10.85	99.99
I-5	10-06-08	10	22.70	357.26	7.00	30.85	18.41	316.01	11.14	-7.38 ^c	88.45
	11-02-08	10	17.80	280.14	9.50	30.15	19.07	97.96	^c	-6.74 ^c	34.97
	11-03-08	10	12.80	201.45	5.88	19.58	13.78	190.54	12.02	-7.96 ^c	94.58
	11-03-08	2	12.80	201.45	5.88	19.58	13.78	382.99	11.08	-11.03	99.99
	11-20-08	10	17.30	272.27	6.90	24.95	15.15	162.56	11.62	-6.96 ^c	59.71
	11-20-08	2	17.30	272.27	6.90	24.95	15.15	206.19	^c	-7.18 ^c	75.73
Dixon Outfall	11-20-08	10	4.43	69.72	4.77	8.37	4.45	98.20	12.59	-12.20	99.99
	12-01-08	10	1.78	28.01	1.81	5.75	4.19	111.05	12.28	-12.75	99.99
	02-06-09	10	4.80	75.54	4.24	12.18	10.02	68.30	12.80	-8.14 ^c	90.42
	02-06-09	2	4.80	75.54	4.24	12.18	10.02	334.78	11.26	-11.80	99.99
	02-23-09	10	3.81	59.96	2.62	8.13	6.91	128.64	12.56	-12.62	99.99
	03-14-09	10	2.50	39.35	2.08	5.24	4.30	105.21	12.75	-12.97	99.99
	04-12-09	10	7.88	124.02	4.79	7.51	6.66	132.69	13.49	-12.34	99.99
	05-13-09	10	13.20	207.74	10.78	8.85	5.91	211.04	12.97	-11.11	99.99
	10-13-09	10	3.28	51.62	4.90	9.42	8.01	78.11	12.06	-11.77	99.99
	11-20-08	10	3.19	50.2	3.69	9.05	4.36	99.57	12.61	-12.60	99.99
Wemme	12-01-08	10	2.30	36.20	1.54	13.60	3.91	66.77	12.58	-12.50	99.99
	01-06-09	10	5.20	81.84	2.56	148.41 ^a	9.59	64.82	11.68	-7.77 ^c	79.20
	01-06-09	2	5.20	81.84	2.56	148.41 ^a	9.59	179.47	10.94	-11.02	99.99
	03-11-09	10	3.84	60.43	5.97	476.59 ^{a,b}	14.09	239.89	10.40	-10.86	99.98
	03-16-09	10	1.90	29.90	2.04	95.94	8.84	^d			
	03-24-09	10	3.02	47.53	2.50	136.34 ^a	9.98	^d			
	03-24-09	2	3.02	47.53	2.50	136.34 ^a	9.98	161.47	10.92	-11.30	99.99
	05-05-09	10	3.10	48.79	1.96	9.61	3.62	56.71	13.06	-12.27	99.99

Notes:

- (a) Mg outside upper limit of ICP-AES calibration
- (b) Ca outside upper limit of ICP-AES calibration
- (c) K_{CuL} was unable to be quantified because Langmuir curve at low [Cu²⁺_{free}] values was not captured in detection window
- (d) Calculated CuL values are not positive or slope for curve was negative
- (e) [Cu²⁺_{diss}] > [L_T] therefore free ionic copper concentration is best estimated by [Cu²⁺_{diss}] - [L_T]

What follows is an examination of the ligand characteristics and $\text{Cu}^{2+}_{\text{free}}$ concentrations determined using the CLE-ACSV method. In addition to summarizing the differences in ligand properties and $\text{Cu}^{2+}_{\text{free}}$ concentrations in composite samples at different sites, the influence of water quality parameters on ligand properties and $\text{Cu}^{2+}_{\text{free}}$ concentrations are examined. These parameters (alkalinity, hardness, dissolved copper concentrations, dissolved organic carbon concentrations) were discussed in detail in Section 2.1. For the reasons outlined above, ligand concentrations and stability constants are compared across sites only at the $10\mu\text{M}$ SA detection window.

Four extremely high hardness samples collected at the Wemme site were not included in statistical calculations (1/06/09, 3/11/09, 3/16/09, and 3/24/09), due to the fact that cation concentrations were outside the calibration region and potentially a seasonal outlier. However, these sites are plotted with a different symbol (open circle) to indicate where they fall in the trends. $\text{Cu}^{2+}_{\text{free}}$ concentrations from I-5 (10/06/08, 11/02/08, 11/20/08) were not used in the statistical analysis, because the analytical window did not fully capture the ligands (see below for further discussion).

4.2.4.1 Ligand Concentration

Figure 4.28 compares the total ligand concentrations determined in composite samples collected at each site. The median ligand concentration determined in I-5 composite samples is 2.92 times (1.03 to 3.72, 95% CI) greater than that found in composite samples from the Wemme site; other site-wise comparisons did not reveal statistically significant differences. Ligand concentrations varied widely (64.8 to 432.7 nM) and indicate that stormwater is a highly heterogeneous mixture that varies in composition from storm to storm and from location to location. This heterogeneity includes variability in the type and concentration of organic ligands present in the runoff. Potential sources of ligands are biological material (leaves, pollen, bacteria, etc.) and anthropogenic derived material (industrial chemicals, petroleum products, partially combusted hydrocarbons, pesticides, etc.). Wemme, Dixon Outfall, and Bend are all sites that would receive both types of organic material, whereas the urban isolation of the I-5 site may result in petroleum products, combustion byproducts and industrial chemicals dominating the mixture.

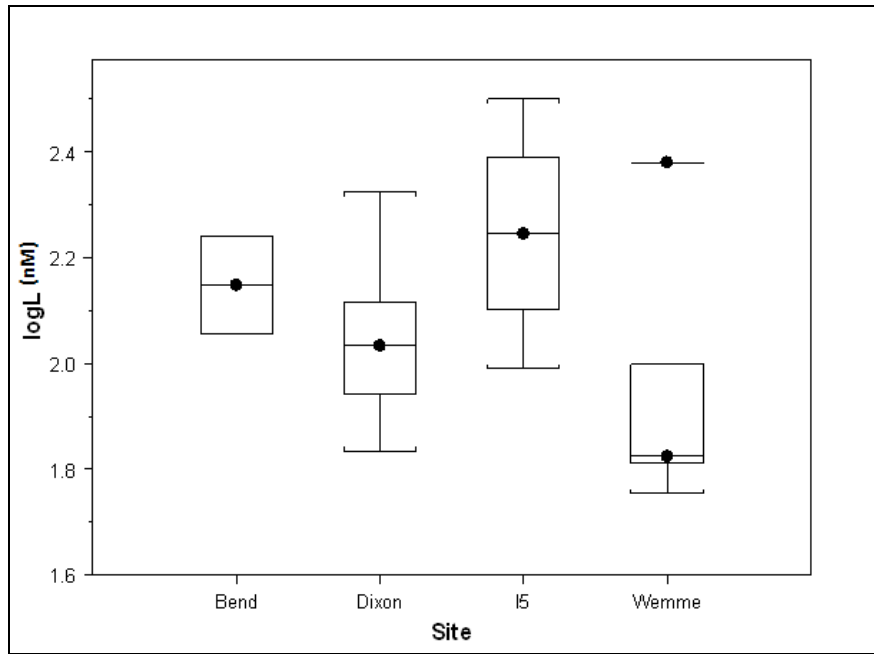


Figure 4.28: Summary of total ligand concentrations determined in composite samples collected at the four sampling sites using the 10 μM SA detection window

Ligand concentration is positively correlated with DOC ($p = 0.005$). As expected, ligand increases as the mass of organics in the system increases. Corroborating the relationship between $\text{Cu}^{2+}_{\text{diss}}$ and DOC in Section 4.1.4, large differences between the magnitude of DOC and ligand concentrations indicate that cation binding sites consist of a small portion of organic molecules present in stormwater. Figure 4.29 shows the relationship between DOC and ligand concentration.

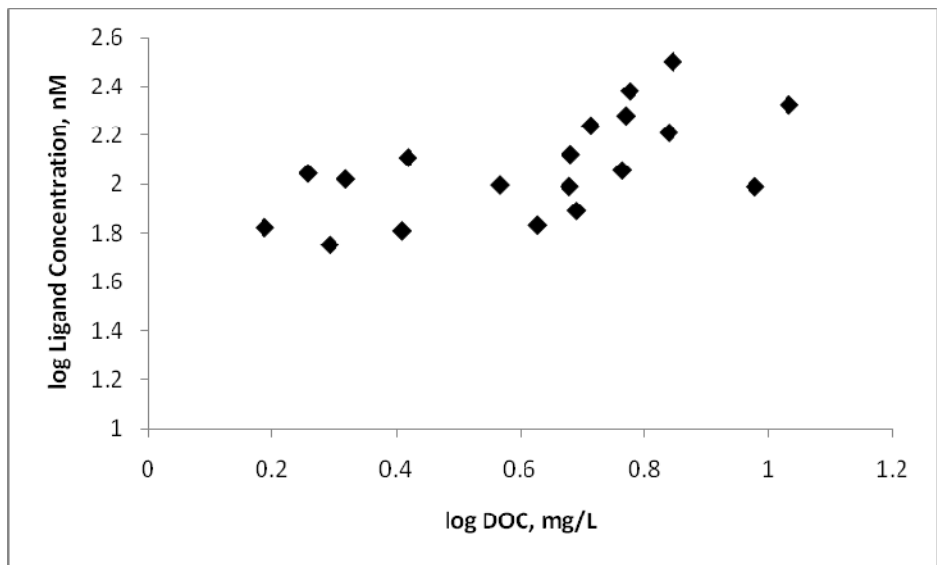


Figure 4.29: Relationship between total ligand concentration and dissolved organic carbon content of composite samples collected at all for sampling sites

4.2.4.2 Conditional Stability Constants

Figure 4.30 compares the conditional stability constants for the Cu-Ligand complexes determined in the composite samples collected at each site. There are significant differences in ligand site binding strengths between Dixon and the I-5 site. The median K'_{CuL} value determined at Dixon Outfall site exceeds that from the I-5 site by 1.1 log units (0.1 to 2.1 log units, 95% CI); no other site-wise comparisons revealed statistically significant differences. Within samples collected at each site, the conditional stability constants were widely variable. This variation can be attributed to the likely difference in type of organic matter present in each sample. For example, one difference could be the relative concentrations of ligands from anthropogenic sources and biogenic sources. This difference is most likely the cause for the significance between the Dixon (varied ligand sources) and I-5 (primarily anthropogenic sources) sites. Composite samples collected at the Wemme site were characterized by an unusually high range of ligand strengths; this may be due to capturing a wide variety of biogenic ligands from different biota, in addition to anthropogenic ligands. Ligand sources at Dixon may have been limited to a few major biotic sources due to a small (relative to the other sites) collection area.

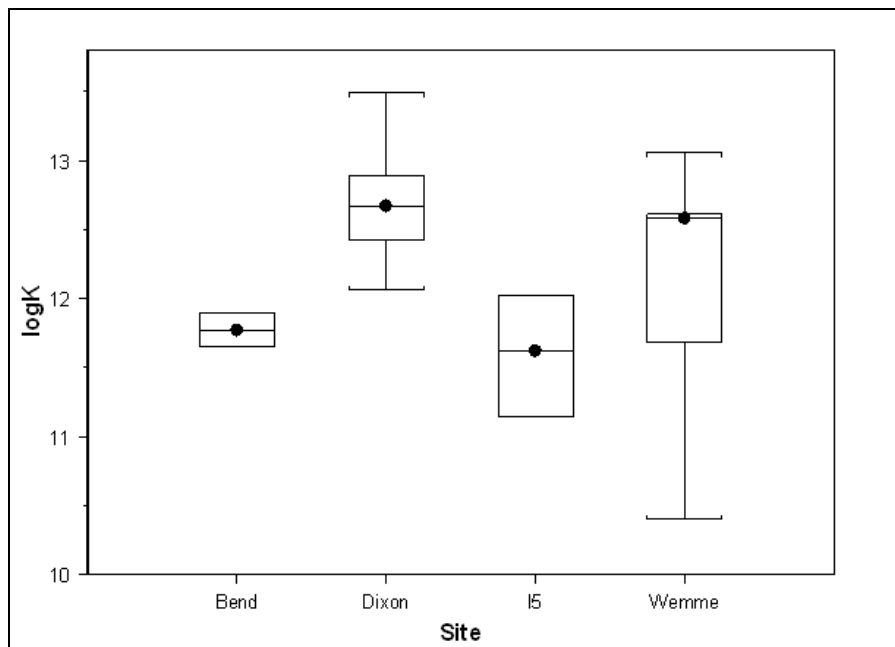


Figure 4.30: Determined stability constants for the CuL complex

As shown in Figure 4.31, there is a negative relationship between K'_{CuL} and hardness ($p = 0.002$). At high hardness concentrations, calcium and magnesium outcompete copper for binding sites on the ligands. As a result, fewer copper atoms are associated with the organic matter at a given total Cu^{2+}_{diss} concentration, leading to a decrease in the conditional stability constant.

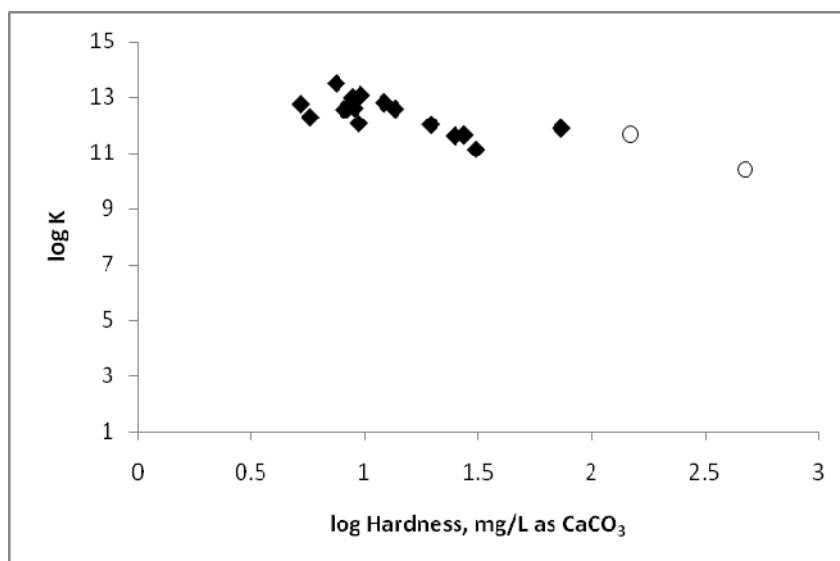


Figure 4.31: Effect of hardness on conditional stability constants (empty circles are high hardness Wemme samples)

4.2.4.3 Free ionic copper Concentrations

The $\text{Cu}^{2+}_{\text{free}}$ concentration can be calculated from the ambient $\text{Cu}^{2+}_{\text{diss}}$ concentration, the total ligand concentration, and the conditional stability constant as described in Section 3.2.10.6. Results from individual samples shown in Table 4.6 reveal that $\text{Cu}^{2+}_{\text{free}}$ concentrations were typically quite low (< 1 ng/L) in stormwater samples. Furthermore, in the majority of cases, the copper was greater than 99.99% complexed by organics in solution. Figure 4.32 compares the $\text{Cu}^{2+}_{\text{free}}$ concentrations determined in composite samples at each site using a 10 μM SA detection window. $\text{Cu}^{2+}_{\text{free}}$ concentrations in composite samples collected from the I-5 site appear to be significantly higher than all other sites. However, statistical comparisons can not be made due to the fact that the measured copper concentrations exceeded the total ligand concentrations in all of the I-5 samples analyzed in the 10 μM SA detection window, leading to an incomplete characterization of the ligands in the sample.

As described above, when large concentrations of $\text{Cu}^{2+}_{\text{diss}}$ and relatively low concentrations of dissolved organic carbon were present in samples, virtually all of the natural ligands were filled with copper at the start of the titrations and added copper immediately began to complex with the added ligand (SA). As a result, the speciation analysis determined a relatively small concentration of strong binding ligands in those samples. For all five I-5 composite samples, and one sample each from Bend, Dixon Outfall and Wemme, the $\text{Cu}^{2+}_{\text{diss}}$ concentration exceeded the total ligand concentration, and a “worst-case” estimate of $\text{Cu}^{2+}_{\text{diss}}$ had to be made.

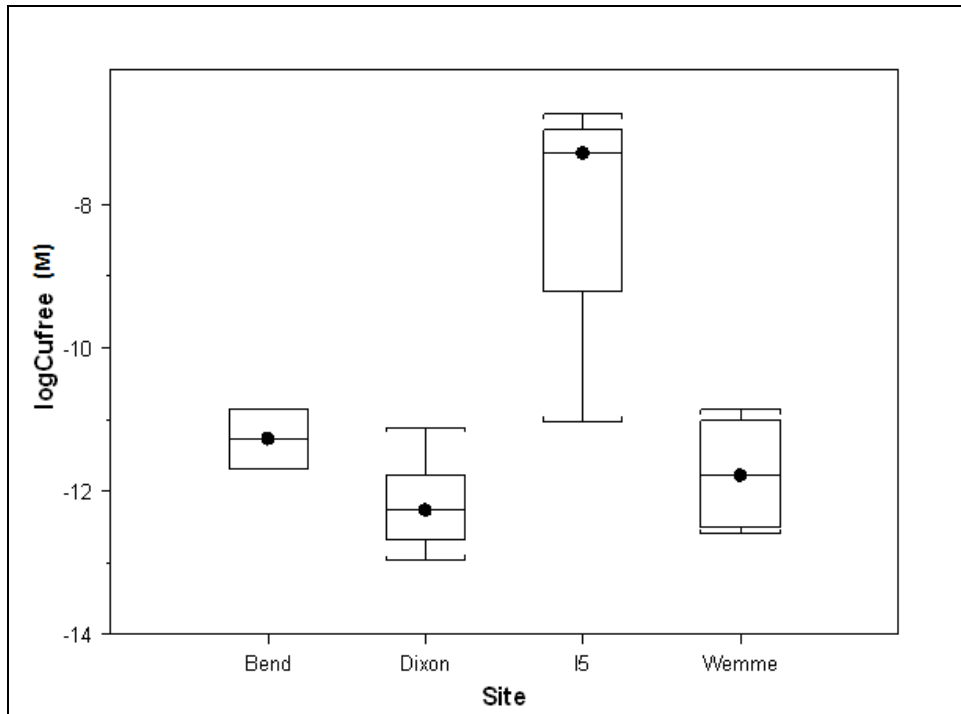


Figure 4.32: Summary of free ionic copper concentrations calculated in composite samples collected at the four sampling sites

As outlined in Chapter 2, the presence of $\text{Cu}^{2+}_{\text{diss}}$ (more specifically, $\text{Cu}^{2+}_{\text{free}}$) can inhibit the olfactory senses of juvenile salmonids. Different studies have reported different effects levels. Sandahl, et al. (2007) determined a negative effect on the olfactory system of juvenile Coho salmon at a nominal concentration of $2 \mu\text{g/L}$ of added $\text{Cu}^{2+}_{\text{diss}}$ (added as CuCl_2 , so virtually all of the $\text{Cu}^{2+}_{\text{diss}}$ was in the free ionic form). The background $\text{Cu}^{2+}_{\text{diss}}$ concentration of the fish hatchery water used in the Sandahl study measured $0.3 \mu\text{g/L}$ and the measured concentration for the $2 \mu\text{g/L}$ $\text{Cu}^{2+}_{\text{diss}}$ addition was $1.9 \pm 0.4 \mu\text{g/L}$. Hecht, et al. (2007) determined a benchmark concentration of $0.59\text{--}2.1 \mu\text{g/L}$ of $\text{Cu}^{2+}_{\text{diss}}$ above background concentrations (defined as $\leq 3 \mu\text{g/L}$) to have a significant effect on the olfaction of unexposed juvenile salmon. In addition, McIntyre, et al. (2008) have shown that the presence of alkalinity, hardness and dissolved organic carbon acts to reduce the neurotoxic effects of $\text{Cu}^{2+}_{\text{diss}}$. Due to the uncertainty in the background concentration of copper used in the Hecht, et al. study, we have adopted the nominal $2 \mu\text{g/L}$ ($10^{-7.5}$ M) concentration of $\text{Cu}^{2+}_{\text{free}}$ as a benchmark for potential toxicity in the following discussion.

$\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$ concentrations for each composite sample are compared to the juvenile Coho salmon toxicity level in Figure 4.33. The $\text{Cu}^{2+}_{\text{diss}}$ concentrations exceed the toxicity threshold of $2 \mu\text{g/L}$ in all but one case. However, analysis of copper speciation (and complexation by organics in particular) reveals that in all samples that were fully characterized (i.e., $[\text{Cu}^{2+}_{\text{diss}}] < [L_T]$), copper was $> 99.9\%$ complexed by organics in the stormwater. As a result, calculated concentrations of $\text{Cu}^{2+}_{\text{free}}$ ranged from 10^{-5} to $10^{-3} \mu\text{g/L}$, well below the effect threshold of

2 µg/L identified by Sandahl, et al. (2007). Of the composite samples where the 10 µM SA detection window (and in one case the 2 µM SA detection window) resulted in a worst-case estimate of the $\text{Cu}^{2+}_{\text{free}}$ concentration, only three samples exceeded the toxicity threshold and all three samples were from the I-5 site. Even the worst case estimates of $\text{Cu}^{2+}_{\text{free}}$ concentrations at the 10 µM SA detection window for the 3/16/2009 Bend sample, the 2/6/2009 Dixon sample, the 11/3/2008 I-5 sample and the 1/6/2009 Wemme sample were below the toxicity threshold. In all but one of these samples, the use of a lower detection window (2 µM SA) revealed large concentrations of weaker ligands and allowed a better estimate of $\text{Cu}^{2+}_{\text{free}}$.

Clearly, these results indicate that the vast majority of $\text{Cu}^{2+}_{\text{diss}}$ is complexed with organics present in highway stormwater runoff. Only samples collected at the urban I-5 site had $\text{Cu}^{2+}_{\text{free}}$ concentrations that exceeded 2 µg/L, and those estimates were worst-case scenarios based on incomplete characterization of the natural ligands. The complexation of copper by organic matter likely renders the copper non-bioavailable to salmonids and would provide some protection against copper toxicity. The results make clear that it is important to consider more than the total or dissolved concentrations of metals in stormwater. The general trends of increased pollution at the urban I-5 site (in terms of total and dissolved copper) do appear to translate to the speciation results, indicating that high-traffic, urban areas are at the greatest risk for copper toxicity.

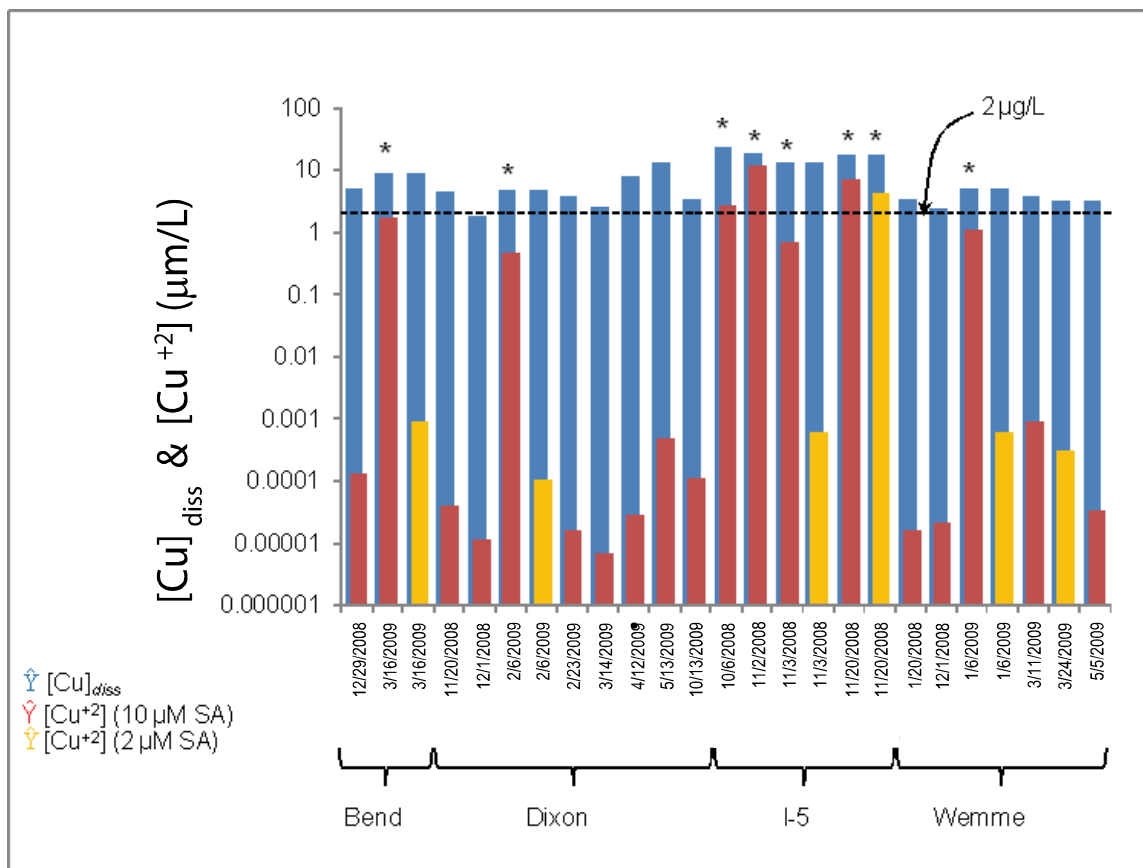


Figure 4.33: Concentrations of total dissolved, and free ionic copper in composite stormwater samples * indicates samples where $[Cu^{2+}]_{diss} > [L_T]$; a “worst case” $[Cu^{2+}]_{free}$ was estimated as $[Cu^{2+}]_{diss} - [L_T]$

The three samples that exceeded the toxicity threshold were all collected from the I-5 site, suggesting that copper toxicity is more likely to be a problem at urban sites where Cu^{2+}_{diss} concentrations are higher. The three exceeding samples had at least 70 nM more of Cu^{2+}_{diss} , higher hardness, and higher DOC than the one I-5 sample that did not exceed the toxicity level. However, as mentioned previously, these three I-5 samples may not have been fully characterized and therefore the Cu^{2+}_{free} concentrations are likely lower than the worst-case scenario reported here.

Although no other samples at any of the sites exceeded the toxicity level, there was a pattern within the sites between high Cu^{2+}_{free} concentrations and other water quality parameters. The 12/29/08 Bend sample with the highest Cu^{2+}_{free} concentration had higher hardness and Cu^{2+}_{diss} concentrations than the only other Bend sample. The 3/11/09 Wemme sample with the highest Cu^{2+}_{free} concentrations had the highest hardness, DOC concentration, and highest Cu^{2+}_{diss} concentrations (except for the 3/24/09 sample) when compared to other Wemme samples. Examining these trends further shows that Cu^{2+}_{free} concentrations are positively correlated with Cu^{2+}_{diss} concentrations ($p < 0.0001$), hardness (p -value is 0.004), DOC ($p < 0.002$), and alkalinity ($p < 0.0001$). These relationships are reflected in Figure 4.34, Figure 4.35, and Figure 4.36, respectively.

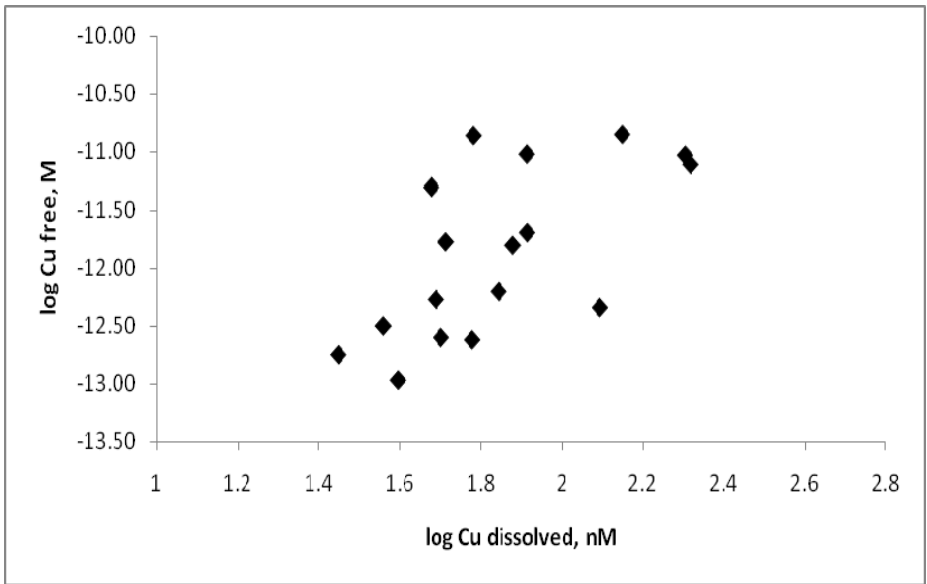


Figure 4.34: Effects of dissolved copper on free ionic copper concentrations

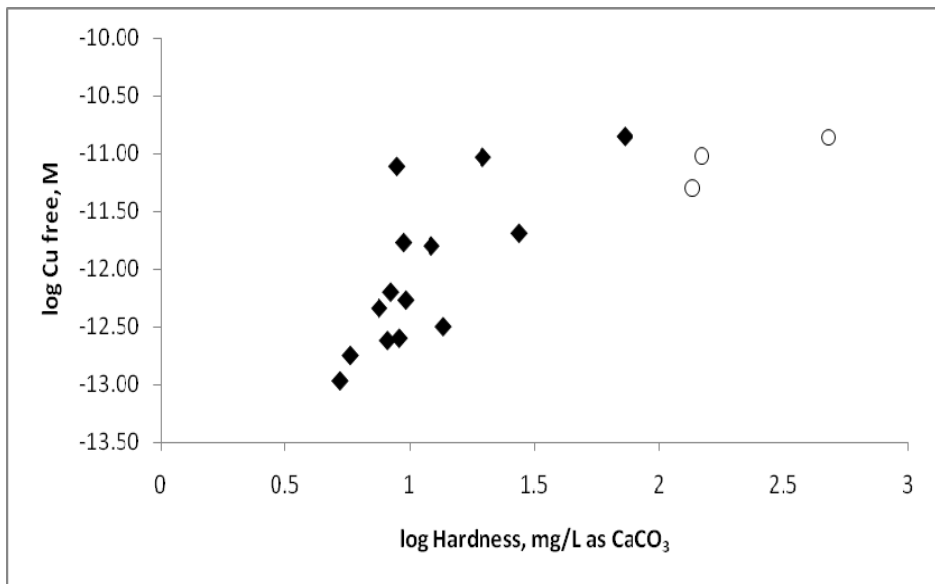


Figure 4.35: Effects of hardness on free ionic copper concentrations (open circles represent high hardness Wemme samples)

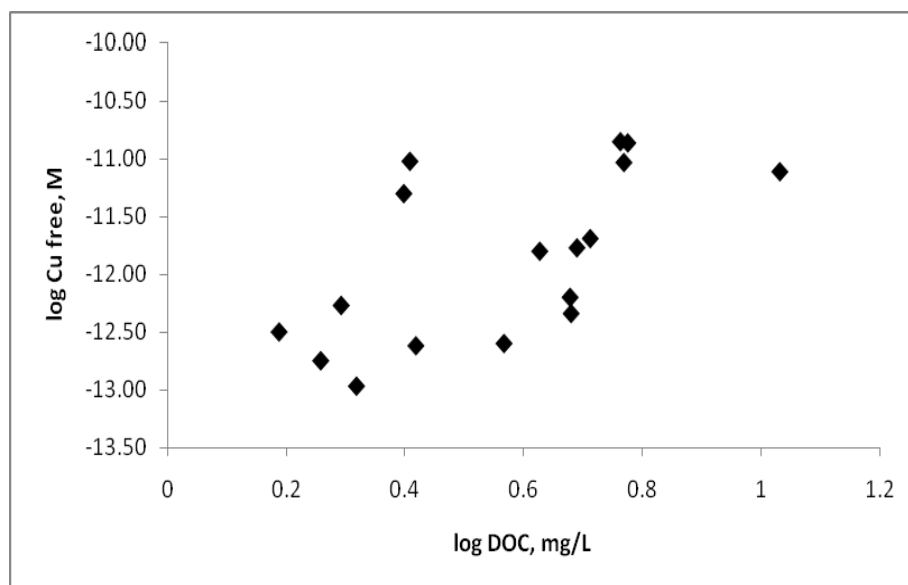


Figure 4.36: Effects of DOC on free ionic copper concentrations

The relationship between $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$ is expected – as $\text{Cu}^{2+}_{\text{diss}}$ increases, so should the species that stem from it. An increase in hardness corresponds with an increase in major cations that can bind with ligand sites on NOM. In turn, this should lower the available number of sites for copper to bind and increase the amount of free ions in solution. The effects of alkalinity were expected to be negative due to the increased complexation of copper by carbonate species, but the co-variation of alkalinity with hardness likely masks those effects.

If $\text{Cu}^{2+}_{\text{free}}$ concentrations were the only indicator for the toxicity of copper, then these results suggest that waters containing high hardness and $\text{Cu}^{2+}_{\text{diss}}$ concentrations are more likely to have toxic levels of $\text{Cu}^{2+}_{\text{free}}$. However, in order for copper to be toxic to organisms, it must first successfully bind with ‘biotic ligand’ sites on the organism. In high hardness waters calcium and magnesium compete with copper for these biotic sites, just as they do for sites on the natural organic ligands. Therefore, the effects of hardness on copper toxicity are likely more complicated than pictured here. Regardless, elevated $\text{Cu}^{2+}_{\text{diss}}$ concentrations in stormwater are a cause for concern, and may be the best *single* indicator for $\text{Cu}^{2+}_{\text{free}}$ and toxicity levels.

The positive relationship between $\text{Cu}^{2+}_{\text{free}}$ and DOC was not expected. An increase in DOC corresponds with an increase in ligand sites, and therefore $\text{Cu}^{2+}_{\text{free}}$ concentrations should decrease due to increased binding with organics. The positive relationship between DOC and $\text{Cu}^{2+}_{\text{diss}}$ (i.e., the fact that more highly polluted waters contain more copper and more DOC) likely overwhelms the relationship between DOC and ligand concentration. There is a weak negative correlation between DOC and K'_{CuL} that may contribute to an overall decrease in the strength of CuL complexes as DOC increases. The co-variation of dissolved organic carbon with $\text{Cu}^{2+}_{\text{diss}}$, the influence of hardness causing cations, and the recognition that not all DOC is equivalent in terms of its ability to bind copper make generalization of the relationships between dissolved organic carbon and $\text{Cu}^{2+}_{\text{free}}$ concentrations difficult. Analytical speciation, like that performed in this

study, and chemical equilibrium modeling (discussed in the next section) are the preferred methods for characterizing the effects of dissolved organic carbon on $\text{Cu}^{2+}_{\text{free}}$ concentrations.

4.2.4.4 Dixon Outfall Speciation Results

A 10 μM SA detection window was appropriate for characterization of the ligands in all but one sample (2/06/09) from Dixon Outfall. $\text{Cu}^{2+}_{\text{diss}}$ was 99.99% complexed with organic ligands in all Dixon Outfall samples. $\text{Cu}^{2+}_{\text{free}}$ concentrations were correspondingly low and did not surpass 2 $\mu\text{g/L}$. Hardness concentrations in the Dixon samples were lower than other sites, which may have contributed to a decrease in calcium/magnesium competition with copper for ligand sites. K'_{CuL} values for Dixon were higher than those at I-5, indicating that sources of DOC at the Dixon site provided stronger copper complexation.

4.2.4.5 I-5 Speciation Results

High $\text{Cu}^{2+}_{\text{diss}}$ concentrations in the I-5 samples led to a truncation of the titration curves. As such, I-5 sites were characterized by low ligand concentrations relative to ambient $\text{Cu}^{2+}_{\text{diss}}$ concentrations within the 10 μM SA detection window. These low ligand concentrations led to $\text{Cu}^{2+}_{\text{free}}$ concentration to be calculated as a worst case scenario in three (of four) samples. Two samples, 11/03/08 and 11/20/08, had sufficient volume to reanalyze at a 2 μM SA detection window. Analysis at the lower detection window revealed the presence of a population of lower strength ligands in both samples. The ligand concentration measured at 2 μM SA in the 11/20/08 sample was still lower than the $\text{Cu}^{2+}_{\text{diss}}$ concentration. High $\text{Cu}^{2+}_{\text{diss}}$ concentrations in the 11/20/08 sample truncated the titration and Langmuir curve and didn't allow determination of the stability constant.

Stability constants for the organic ligands at the I-5 site were lower than those at Dixon Outfall. DOC concentrations in I-5 samples were also higher than those at Dixon and Wemme. This suggests that anthropogenic DOC at the I-5 site, such as petroleum and industrial chemicals, forms only weak(er) complexes with copper. 34.97% or more of the $\text{Cu}^{2+}_{\text{diss}}$ in the samples was complexed with the organic ligands. However, for all of the samples analyzed at the 10 μM SA detection window, this was a worst-case estimate. All but one of the worst-case estimates for $\text{Cu}^{2+}_{\text{free}}$ exceeded 2 $\mu\text{g/L}$. Hardness concentrations at the I-5 site were not excessively high (as compared to those at Wemme). DOC concentrations were the highest of all the sites, but $\text{Cu}^{2+}_{\text{free}}$ concentrations exceeded all other sites based on the worst-case estimates. These results suggest that the elevated $\text{Cu}^{2+}_{\text{diss}}$ concentration at the I-5 site were the leading cause of differences in $\text{Cu}^{2+}_{\text{free}}$ concentrations.

4.2.4.6 Bend Speciation Results

Through analysis at 10 μM of SA, ligand concentration and stability constants at Bend were not significantly different from the other sites. One sample (3/16/09) contained more $\text{Cu}^{2+}_{\text{diss}}$ than ligand sites. Further investigation with the 2 μM SA

window showed that weaker ligands were present. Overall, at least 99.99% of $\text{Cu}^{2+}_{\text{diss}}$ in both samples was complexed with organic ligands. The collection of more samples for Bend would allow a fuller characterization of the site; as it stands, the low number of samples allows for limited conclusions.

4.2.4.7 *Wemme Speciation Results*

K'_{CuL} values at Wemme varied widely, ranging from $10^{10.40}$ to $10^{13.06}$, indicating that a variety of organic material types were present in the stormwater. A high influx of magnesium and chloride in the stormwater occurred during mid- to late winter. This hardness spike is due to road salt (MgCl_2) additions to aid driving in ice/snow. Organic ligands in stormwater collected at Wemme were characterized well in a $10 \mu\text{M}$ SA detection window. Of the samples successfully measured, only one (3/11/09) fell below 99.99% copper complexation. $\text{Cu}^{2+}_{\text{free}}$ concentrations were higher than in Dixon Outfall samples, but otherwise were low, not surpassing $2 \mu\text{g/L}$ in any samples. Extremely high hardness (476.6 mg/L as CaCO_3) corresponded to the elevated $\text{Cu}^{2+}_{\text{free}}$ concentration in the 3/11/09 storm.

K'_{CuL} and $[L]$ could not be quantified for two samples (3/24/09 and 3/16/09) at the $10 \mu\text{M}$ SA window due to misleading results for their Langmuir curve fits. The Langmuir curve fit to the 3/24/09 sample reached a plateau briefly before declining. This formed an overall negative slope for the Langmuir isotherm. This negative slope was caused by the sensitivity decreasing as the titration progressed. Approach of electrode saturation was the likely cause of this drop in sensitivity. The 3/16/09 sample resulted in negative calculated values for CuL. From Equation (3-5), an overestimation of $[\text{CuSA}_x]$ can lead to negative CuL concentrations if $[\text{CuSA}_x]$ exceeds $[\text{Cu}^{2+}_{\text{diss}}]$. Overestimation of $[\text{CuSA}_x]$ can occur in the presence of sufficient surfactants; as titration sensitivity decreases with increasing surfactant concentration, leading to an overestimation of $[\text{CuSA}_x]$ (see Equation (3-6)). Using an internal slope (sensitivity) can correct for this suppression (Kogut and Voelker 2001), but tests on Willamette River water revealed that correction for surfactants has a limit. Negative CuL concentrations indicate an extreme case of surfactant suppression.

4.2.4.8 *Comparison to Previous Studies*

Mean $\text{Cu}^{2+}_{\text{diss}}$ concentrations in stormwater samples were typically greater than those measured in previous fresh/seawater studies; in some cases, $\text{Cu}^{2+}_{\text{diss}}$ concentrations were orders of magnitude larger than those in typical surface waters. These trends were not surprising, given the increased levels of pollutants in stormwater with respect to surface freshwater and rainwater. Mean $\text{Cu}^{2+}_{\text{free}}$ concentrations were also generally greater than those measured in previous freshwater/seawater studies. No free copper concentrations in the fresh/seawater studies exceeded $2 \mu\text{g/L}$. Differences in pH and ionic strength prevent any comparison of K'_{CuL} and ligand concentrations between the studies.

Buck and Bruland (2005), noted that the copper complexation capacity of one of their sites at Dumbarton Bridge was near 108 nM of $\text{Cu}^{2+}_{\text{diss}}$ – over double the measured concentration of $\text{Cu}^{2+}_{\text{diss}}$. The implication of these results is the possibility that fresh/seawater sites may have substantial capacity to complex copper spikes and/or point source pollution from stormwater. Therefore, it is important to examine the characteristics of the receiving waters (e.g., organic matter type and concentration) to fully evaluate the potential for copper toxicity. Elevated dissolved and $\text{Cu}^{2+}_{\text{free}}$ concentrations are likely to be higher at the source of the pollution, but will be diluted as the stormwater mixes with the surface water. Furthermore, copper may re-equilibrate with the ligands present in the surface water. All of these processes must be considered when evaluating the potential for copper toxicity from highway stormwater runoff. What the results from this study indicate is that in the stormwater itself (similar to many natural waters), there is a large complexation capacity, and the majority of the copper is bound with organic matter.

4.2.5 Intrastorm and First Flush Results

The speciation results determined with 10 μM SA for all samples (grab, first flush, and composite) collected at the Dixon site are presented in Table 4.7; as in Table 4.6, water quality parameters are also included. In general, speciation analysis of the first-flush and grab samples was hampered by the high $\text{Cu}^{2+}_{\text{diss}}$ concentrations and elevated levels of other pollutants (e.g., surfactants, etc.) in these samples, which created problems for the analytical method. The majority of first flush and intra-storm samples did not yield reliable information for conditional stability constants or $\text{Cu}^{2+}_{\text{free}}$ concentrations; those that did included the first flush and intra-storm samples collected on 11/20/2008, and the #4 and #20 samples from the 10/13/2009 storm. These samples had low hardness, $\text{Cu}^{2+}_{\text{diss}}$, and DOC concentrations. Conversely, the first flush samples that did not yield copper speciation information had high $\text{Cu}^{2+}_{\text{diss}}$ concentrations (roughly equivalent or exceeding I-5 composite samples), which led to saturated ligands in the 10 μM SA detection window. Those first flush samples with sufficient volume were also tested at 2 μM SA, but analyses did not yield additional information due to negative CuL concentrations or negatively sloped Langmuir equation fits. This issue was likely due to a marked increase in surfactants or other compounds in the first flush samples that interfered with the mercury electrode.

Table 4.7: Speciation results for first flush, intrastorm, and composite samples from Dixon Outfall

Storm	Type	SA	[Cu ²⁺ _{diss}]		DOC	Hardness	Alkalinity	[LT]	log K'CuL	log [Cu ²⁺ _{free}]	Cu Complexation
			μM	μg/L							
11/20/2008	Composite	10	4.43	69.72	4.77	8.37	4.45	98.2	12.59	-12.20	99.99
11/20/2008	First Flush	10	9.02	141.96	12.52	19.1	7.09	158	12.45	-11.49	99.99
11/20/2008	#3+4	10	2.55	40.13	2.59	6.13	3.18	43.4	13.08	-11.99	99.99
12/1/2008	Composite	10	1.78	28.01	1.81	5.75	4.19	111.05	12.28	-12.75	99.99
12/1/2008	First Flush	10	16.43	258.58	14.2	41.04	13.56	216	12.91	-7.37 ^c	83.50
2/6/2009	Composite	10	4.8	75.54	4.24	12.18	10.02	68.3	12.80	-8.14 ^e	90.42
2/6/2009	Composite	2	4.8	75.54	4.24	12.18	10.02	334.78	11.26	-11.80	99.99
2/6/2009	First Flush	10	12.2	192.01	15.57	63.11	20.58	137	^c	-7.26 ^e	71.38
2/23/2009	Composite	10	3.81	59.96	2.62	8.13	6.91	128.64	12.56	-12.62	99.99
2/23/2009	First Flush	10	20.9	328.93	18.45	47.06	18.55	285	^c	-7.36 ^e	86.73
3/14/2009	Composite	10	2.5	39.35	2.08	5.24	4.3	105.21	12.75	-12.97	99.99
3/14/2009	First Flush	10	17.5	275.42	16.02	52.23b	9.75	224	11.91 ^c	-7.29 ^e	81.38
4/12/2009	Composite	10	7.88	124.02	4.79	7.51	6.66	132.69	13.49	-12.34	99.99
4/12/2009	First Flush	10	35.6	560.28	27.44	27.24	10.21	535	13.10 ^c	-7.60 ^e	95.52
5/13/2009	Composite	10	13.2	207.74	10.78	8.85	5.91	211.04	12.97	-11.11	99.99
5/13/2009	First Flush	10	30.5	480.01	37	34.27	12.4	479	12.92 ^c	-9.00 ^e	99.79
5/13/2009	#4	10	24.5	385.58	26.08	20.87	9.27	413	12.88	-11.70	99.99
9/29/2009	First Flush	10	10.3	162.10	16.75	28.29	6.4	118.69	12.56 ^c	-7.36 ^e	73.07
9/29/2009	#2	10	7.28	114.57	9.79	11.15	4.35	40.6	12.98 ^c	-7.13 ^e	35.41
10/13/2009	Composite	10	3.28	51.62	4.9	9.42	8.01	78.11	12.06	-11.77	99.99
10/13/2009	First Flush	10	11.5	180.99	15.79	28.1	11.2	36.7	^c	-6.84 ^e	20.14
10/13/2009	#4	10	4.58	72.08	5.26	8.66	9.9	93.1	12.13	-11.54	99.99
10/13/2009	#5	10	5.2	81.84	8.58	16.45	13.7	37.3	12.29 ^c	-7.35 ^e	45.42
10/13/2009	#11	10	2.37	37.30	4.25	7.53	7.58	35.7	12.59	-8.81 ^e	95.85
10/13/2009	#17	10	0.97	15.27	2.81	5.54	6.34	12	12.65	-8.49 ^e	78.80
10/13/2009	#20	10	1.36	21.40	3.6	7.55	5.73	61.2	12.01	-12.28	99.99

Notes:

- (a) Mg outside upper limit of ICP-AES calibration
- (b) Ca outside upper limit of ICP-AES calibration
- (c) KCuL was unable to be quantified or suspect because Langmuir curve at low Cu²⁺_{free} values was not captured in detection window
- (d) Calculated CuL values are not positive or slope for curve was negative
- (e) [Cu²⁺_{diss}] > [LT] therefore Cu²⁺_{free} concentration is best estimated by [Cu²⁺_{diss}] - [LT]

4.2.5.1 Ligand Concentrations in Dixon Outfall Samples

Organic ligand concentrations determined for the first flush samples exceeded the composite concentrations at Dixon Outfall in all but one sample (10-13-09). On average, the first flush samples had ligand concentrations 1.8 times higher than the composite samples for the same storm (1.09 to 2.98 times, 95% CI). This difference is significant ($p = 0.0286$). Figure 4.37 and Figure 4.38 compare the ligand concentration within each storm and the overall differences between first flush and composite samples, respectively. The higher organic ligand concentrations in the first flush samples are related to the elevated DOC concentrations relative to the composite samples.

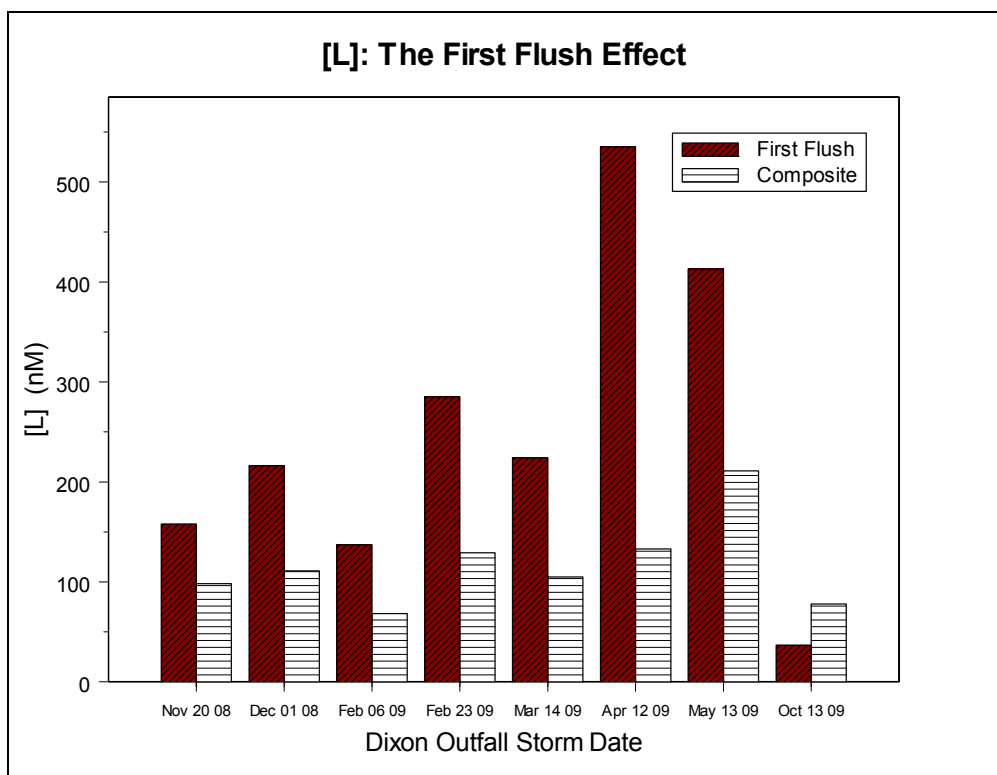


Figure 4.37: Ligand concentrations for first flush and composite samples at Dixon Outfall

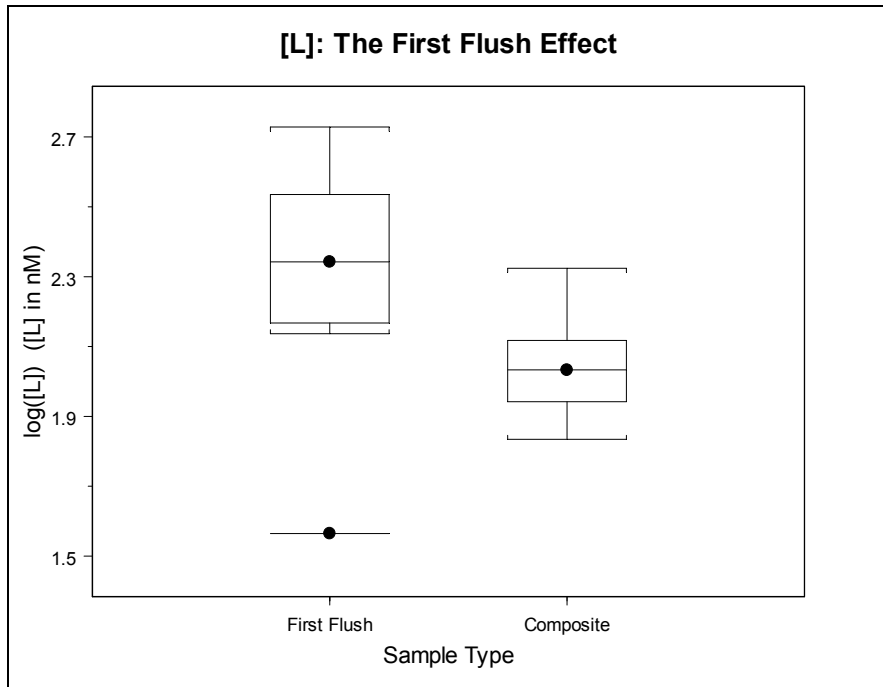


Figure 4.38: Comparison between $[L_T]$ values for first flush and composite samples

As was the case with composite samples, $[L_T]$ was positively associated with DOC ($p = 0.0006$). On average, a doubling in DOC was associated with a 1.61-fold increase in $[L_T]$ (1.26 – 2.06, 95% CI). This relationship between $[L_T]$ and DOC in first flush and composite samples is more significant and greater in magnitude than with composite samples alone. This implies that organics collected at the beginning of a storm may have a greater number of copper binding sites available.

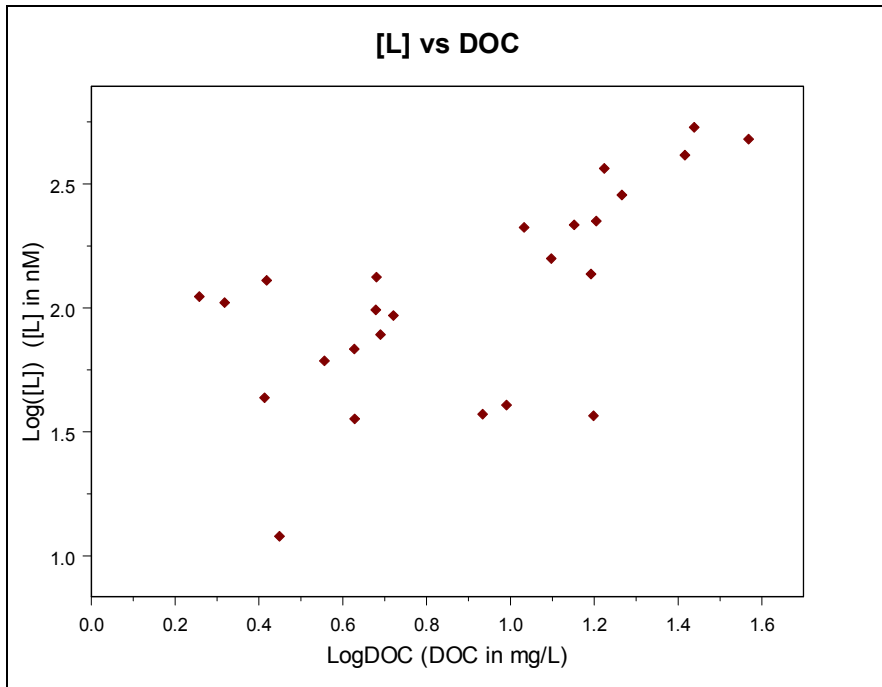


Figure 4.39: Relationship between $[L_T]$ and DOC for Dixon Outfall samples

Figure 4.40 shows the relationship between $[L_T]$ and hardness for all the Dixon Outfall samples. Considering the log-transformation, $[L_T]$ was positively associated with hardness ($p = 0.0034$). On average, a doubling in hardness was associated with a 1.60-fold increase in $[L_T]$ (1.19 – 2.16, 95% CI). Hardness should not be directly related to $[L_T]$; therefore the positive association is likely due to major cations (Ca, Mg, etc) and organic matter (DOC) being flushed into the stormwater together.

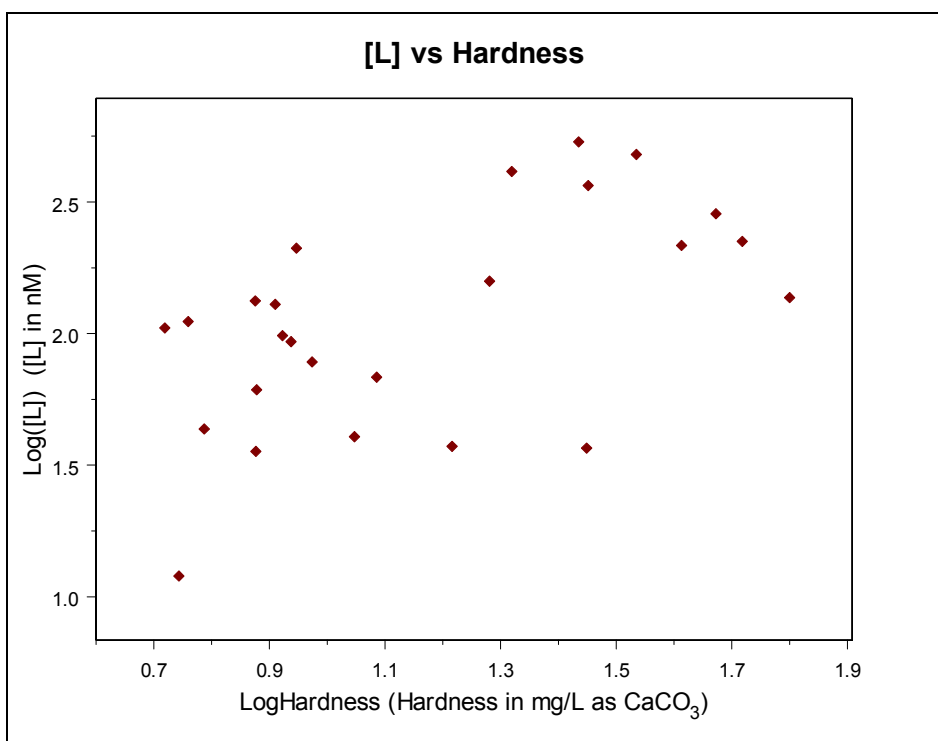


Figure 4.40: Relationship between $[L_T]$ and hardness for Dixon Outfall samples

4.2.5.2 Free Ionic Copper Concentrations in First Flush and Discrete Samples

Calculated $\text{Cu}^{2+}_{\text{free}}$ concentrations in 6 of the 9 first flush samples exceeded $2 \mu\text{g/L}$. In each case, the $\text{Cu}^{2+}_{\text{free}}$ concentration was a worst case estimate, due to the fact that the ligands were saturated at the $10 \mu\text{M}$ SA detection window. Attempts to characterize the samples at the $2 \mu\text{M}$ SA detection window were inhibited by the signal suppression by surfactants or other constituents in the samples. Only 2 of the 8 discrete samples collected during individual storms exceeded the toxicity threshold. Again, these estimates were worst case estimates obtained at the $10 \mu\text{M}$ SA detection window. In every sample where the ligands were fully characterized at the $10 \mu\text{M}$ SA detection window, the $\text{Cu}^{2+}_{\text{free}}$ concentrations were well below the toxicity threshold.

As with the composite samples, trends in the $\text{Cu}^{2+}_{\text{free}}$ concentrations tracked well with the relative concentrations of $\text{Cu}^{2+}_{\text{diss}}$ present in the samples. First flush samples had significantly more $\text{Cu}^{2+}_{\text{diss}}$ than the composite samples and discrete samples collected over the course of individual storms. These elevated $\text{Cu}^{2+}_{\text{diss}}$ concentrations were likely the reason that the ligands in these samples could not be fully characterized. Based on these results it does appear that the risk of copper toxicity from the release of highway stormwater at the beginning of a storm poses a greater risk than event mean concentrations, or runoff discharged later in a storm. However, it is likely that even in those samples, a substantial fraction (greater than that reported in Table 4.7) of the copper is bound with organic matter in these samples. Unfortunately, the heterogeneous nature of the

dirtier first-flush samples prevented accurate characterization of the stormwater organics in this study and limits the ability to make firm statements about the likely toxicity of first flush samples.

4.2.6 Chemical Equilibrium Modeling

Speciation modeling using Visual MINTEQ was performed on all samples for which concentrations of all cations (including trace metals), anions, and DOC were quantified. Initially, all 48 such samples were modeled using the Gaussian DOM Model; these included 22 composite samples from the various sites, 8 first flush samples, 7 grab samples, and 10 flow-weighted samples from Dixon Outfall. Subsequently, more sophisticated DOM models (NICA-Donnan and SHM) were utilized to examine the speciation in composite samples. Results from the chemical equilibrium models were compared with analytical determinations of $\text{Cu}^{2+}_{\text{free}}$. This analysis was limited to the composite samples because of the larger uncertainty associated with the analytical determination of speciation in the first flush and flow-weighted samples at the Dixon Outfall site.

4.2.6.1 Speciation Modeling with the Gaussian DOM Model

Results of the speciation analysis using the Gaussian DOM model predicted that the concentrations of the cupric ion (Cu^{2+}), the modeled Cu-DOM complex, CuOH^+ and CuCO_3 accounted for over 99% of the copper species in all but one sample (Wemme 3/11/09). The Cu-DOM complex was typically the most abundant species, accounting for a median of 86.5% of copper species in the modeled stormwaters. Modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations ranged from 0.086 to 2.55 $\mu\text{g/L}$ with a median of 0.53 (1.36-40.1 nM, median of 8.33 nM). $\text{Cu}^{2+}_{\text{free}}$ accounted for a range of 2.4- 35% of the $\text{Cu}^{2+}_{\text{diss}}$ in the samples, with a median of 8.4%. Samples with elevated concentrations of $\text{Cu}^{2+}_{\text{free}}$, and higher percent $\text{Cu}^{2+}_{\text{free}}$ coincided with high hardness concentrations, especially at the Bend and Wemme sites. As mentioned previously, higher hardness at these sites coincided with the application of MgCl_2 road salts. The effect of hardness on copper speciation is more thoroughly examined in subsequent sections. Complete results from the copper speciation modeling effort are provided in Appendix A.4.

Overall, the results of the Gaussian DOM modeling suggested that $\text{Cu}^{2+}_{\text{free}}$ concentrations were quite low and that the majority of $\text{Cu}^{2+}_{\text{diss}}$ was bound with organic matter in highway stormwater runoff. Comparing the modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations with the 2 $\mu\text{g/L}$ toxicity criterion, only one of the 48 samples showed an exceeding Cu^{2+} concentration (the I-5 10/6/08 composite).

4.2.6.2 Site Comparisons

Figure 4.41 presents the modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations at the four sites. For reference, the 2 $\mu\text{g/L}$ toxicity threshold equates to a $\log[\text{Cu}^{2+}_{\text{free}}]$ value of 1.5. The trends in modeled $\text{Cu}^{2+}_{\text{free}}$ are similar to the trends in measured $\text{Cu}^{2+}_{\text{diss}}$ at the four sites. As with $\text{Cu}^{2+}_{\text{diss}}$, the I-5 site showed consistently higher concentrations of $\text{Cu}^{2+}_{\text{free}}$ than the other three sites. The similarity in these plots underscores the direct relationship between $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. Furthermore, results suggest that

the elevated DOC concentrations in the I-5 samples were not high enough to increase in the copper complexation capacity and keep the $\text{Cu}^{2+}_{\text{free}}$ concentrations low. The most obvious difference between Figure 4.1 ($\text{Cu}^{2+}_{\text{diss}}$ concentrations) and Figure 4.41 (modeled $\text{Cu}^{2+}_{\text{free}}$) is the elevated and highly varied concentrations of $\text{Cu}^{2+}_{\text{free}}$ in the Wemme samples. The peak $\text{Cu}^{2+}_{\text{free}}$ of the Wemme samples approaches I-5 levels, while the lowest concentration of $\text{Cu}^{2+}_{\text{free}}$ is below some Dixon Outfall samples. Reasons for these trends are discussed below.

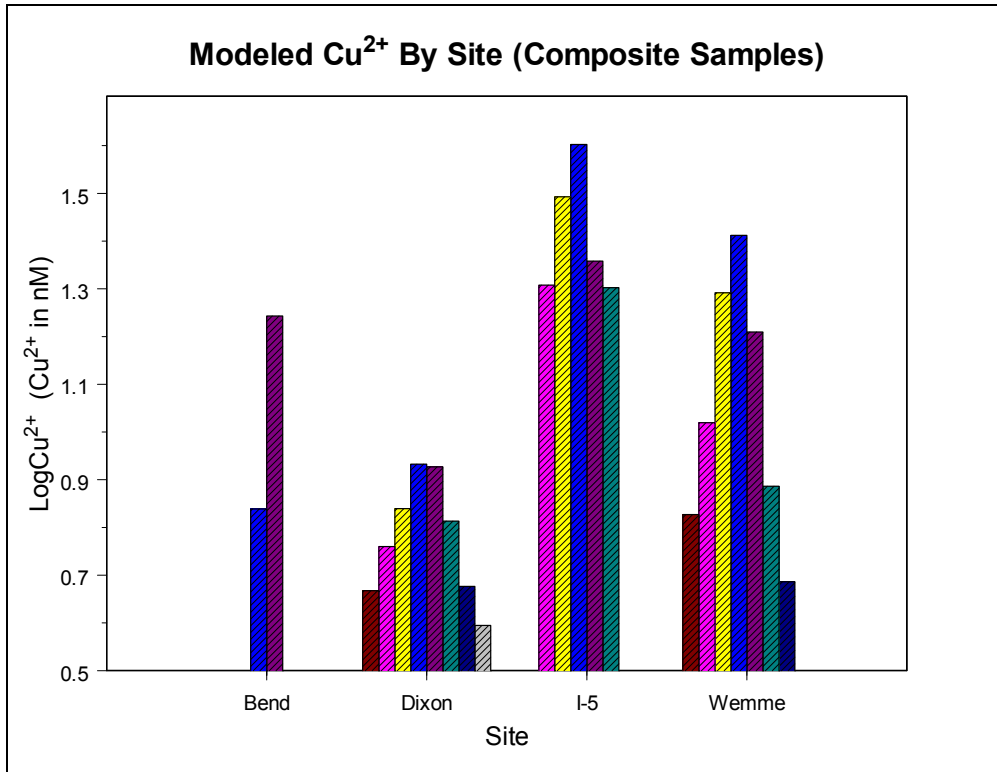


Figure 4.41: Modeled free ionic copper concentrations in composite samples

Although not as important as the overall concentration of $\text{Cu}^{2+}_{\text{free}}$, examining the percentage of $\text{Cu}^{2+}_{\text{free}}$ provides insight into instances where copper toxicity might become a problem. Figure 4.42 displays the percentage of $\text{Cu}^{2+}_{\text{free}}$ in the composite samples at the four sites. Modeling results predict that samples from Bend, I-5, and Dixon Outfall have about 9% of the $\text{Cu}^{2+}_{\text{diss}}$ in the free ionic form, while the Wemme subset displays a wide range of $\text{Cu}^{2+}_{\text{free}}$ percentages with a much higher median. From these data, it is evident that the Wemme samples exhibited a much larger and wider distribution of percent $\text{Cu}^{2+}_{\text{free}}$. Further analysis shows that four of the Wemme composite samples contained high levels of hardness, and this significantly affected the copper speciation of these samples. On average, these four samples contained six times the concentration of calcium and over 20 times the amount of magnesium compared to the other three Wemme composite samples. The increased calcium and magnesium concentrations resulted in hardness that was 10 or more times greater than the other Wemme

composites and caused an increase in the percent of $\text{Cu}^{2+}_{\text{free}}$ in solution. Examining the species distribution of DOM in the speciation model agrees with this assessment. The high hardness Wemme samples did not exhibit vastly different copper or DOC concentrations in comparison to the low hardness Wemme samples. The high hardness samples contained an average of $0.63 \mu\text{g/L}$ more copper and 0.87 mg/L more DOC. However, Mg-DOM made up 6.2-15.2% of the DOM species in the high hardness samples, but only 0.8-2.4% in the low hardness samples. Magnesium, along with a small contribution from calcium, occupied binding sites on the modeled organic molecules and reduced the free DOM from 76-79% in the low hardness samples to 66-68% in the high hardness samples, thereby reducing the potential for DOM to complex $\text{Cu}^{2+}_{\text{free}}$.

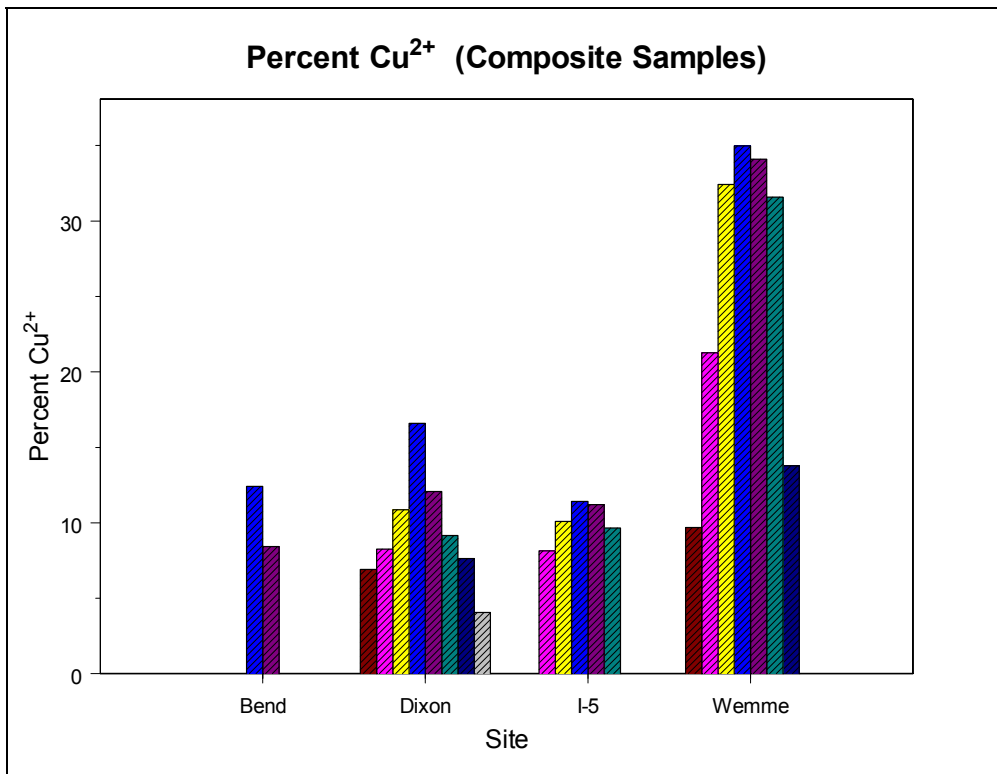


Figure 4.42: Modeled percentage of dissolved copper present as free Cu^{2+} in composite samples

4.2.6.3 The First Flush Effect

The first flush effect on modeled $\text{Cu}^{2+}_{\text{free}}$ is similar to the first flush effect witnessed on $\text{Cu}^{2+}_{\text{diss}}$ concentrations in Section 4.1.2. Figure 4.43 compares $\text{Cu}^{2+}_{\text{free}}$ concentrations in first flush and composite samples for the 8 storms collected at the Dixon Outfall site. In all cases, first flush samples were predicted to have higher levels of $\text{Cu}^{2+}_{\text{free}}$ than their respective composite samples. The percentage of $\text{Cu}^{2+}_{\text{diss}}$ present as $\text{Cu}^{2+}_{\text{free}}$ in the two sample types is shown in Figure 4.44. Interestingly, a lower percentage of $\text{Cu}^{2+}_{\text{free}}$ exists in first flush samples as compared to composite samples. The factors that most affect copper species distribution in these samples are DOC and hardness. First flush samples

are characterized by high concentrations of most runoff constituents, including hardness (Ca and Mg), DOC, and $\text{Cu}^{2+}_{\text{diss}}$. The fact that lower percentages of $\text{Cu}^{2+}_{\text{free}}$ are present in first flush samples reveals that, in the model, the increased concentration of DOM overwhelms the effects of increased concentrations of divalent cations, which compete with $\text{Cu}^{2+}_{\text{free}}$ for binding sites on organics. Therefore, it is likely that the increased $\text{Cu}^{2+}_{\text{free}}$ seen in Figure 4.43 is attributable to higher $\text{Cu}^{2+}_{\text{diss}}$ concentrations, and not competition from calcium and magnesium.

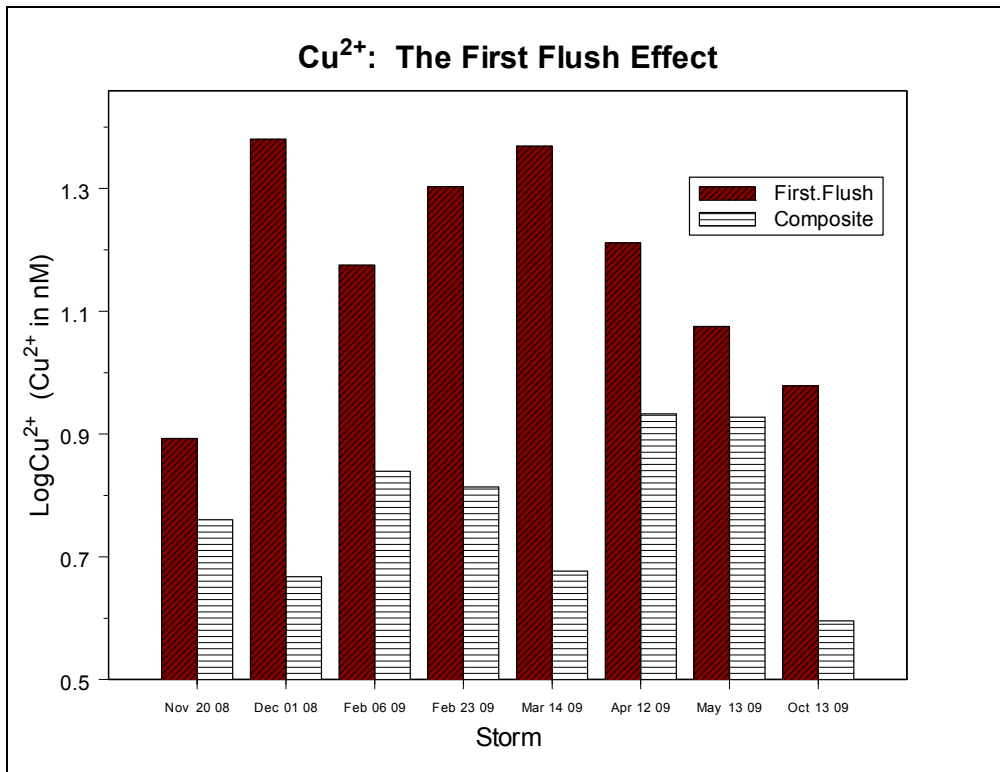


Figure 4.43: The first flush effect on free ionic copper

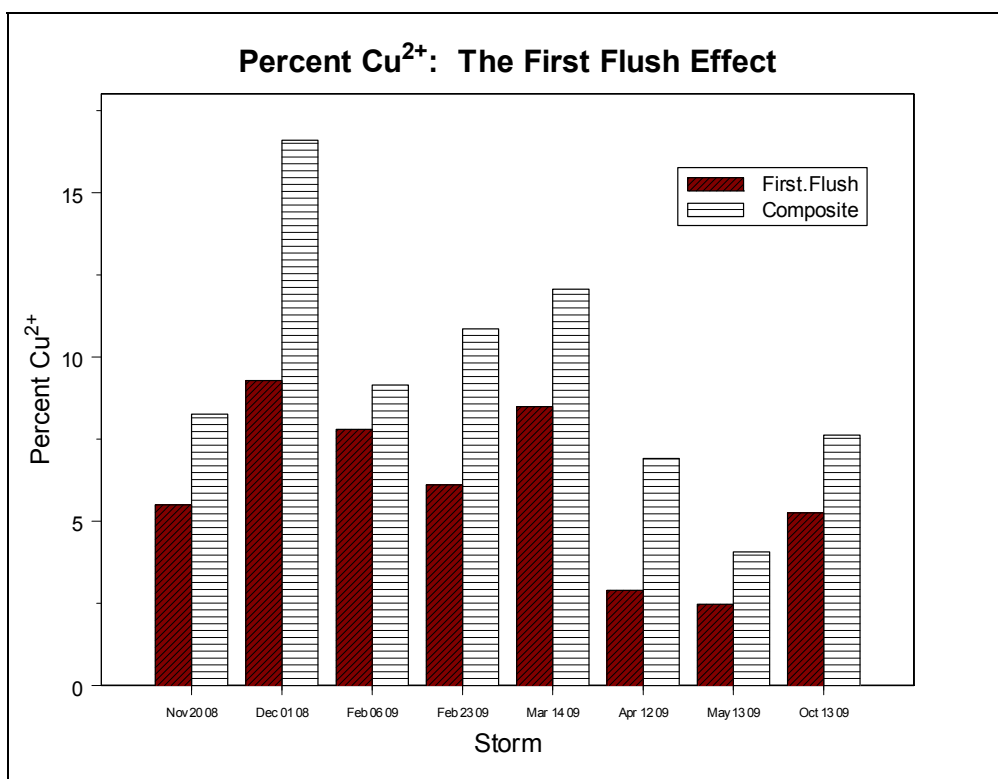


Figure 4.44: The first flush effect on Percent free ionic copper

4.2.6.4 Intra-Storm Copper Variations

Runoff samples from the 10/13-10/14/09 storm at Dixon Outfall were fully quantified and modeled for their speciation using the Gaussian DOM model. The results of that analysis are summarized in Figure 4.45. The storm hydrograph is shown in the primary vertical axis, while concentrations of $\text{Cu}^{2+}_{\text{free}}$, Cu-DOM, and the baseline salmonid $\text{Cu}^{2+}_{\text{free}}$ toxicity levels reported from Sandahl (2007) ($2 \mu\text{g/L}$, 31.5 nM) are on the secondary vertical axis. The first flush Cu-DOM concentration was 162 nM but not shown due to space constraints. The concentration of CuOH^+ ranged from 0.4 nM (in the 5th and 6th samples) to 6.50 nM (in the 3rd sample) while the concentration of CuCO_3 ranged from 0.4 nM (in the 5th sample) to 3.3 nM (in the 1st sample); these were also not graphed due to space constraints.

None of the samples eclipsed the $2 \mu\text{g/L}$ toxicity level. The trend in modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations was similar to that of measured dissolved concentrations shown in Figure 4.18. The similarity of Figure 4.18 and Figure 4.45 underscores the relationship between DOC, $\text{Cu}^{2+}_{\text{diss}}$, and $\text{Cu}^{2+}_{\text{free}}$. The highest concentration of $\text{Cu}^{2+}_{\text{free}}$ was found in the first flush sample, and the concentration generally decreased over the course of the storm. The breaks in this storm (e.g., between approximately 19:00 and 23:00) that appeared to result in small intra-storm flushes of $\text{Cu}^{2+}_{\text{diss}}$ also produced slight increases in $\text{Cu}^{2+}_{\text{free}}$, notable in the 3rd and 6th samples collected in this storm. The decrease in $\text{Cu}^{2+}_{\text{free}}$ over the course of this storm supports the idea that highway runoff early in a storm is potentially more

toxic to aquatic life than runoff later on in the storm. However, in this case, even in the first flush, $\text{Cu}^{2+}_{\text{free}}$ concentrations are predicted to be very low.

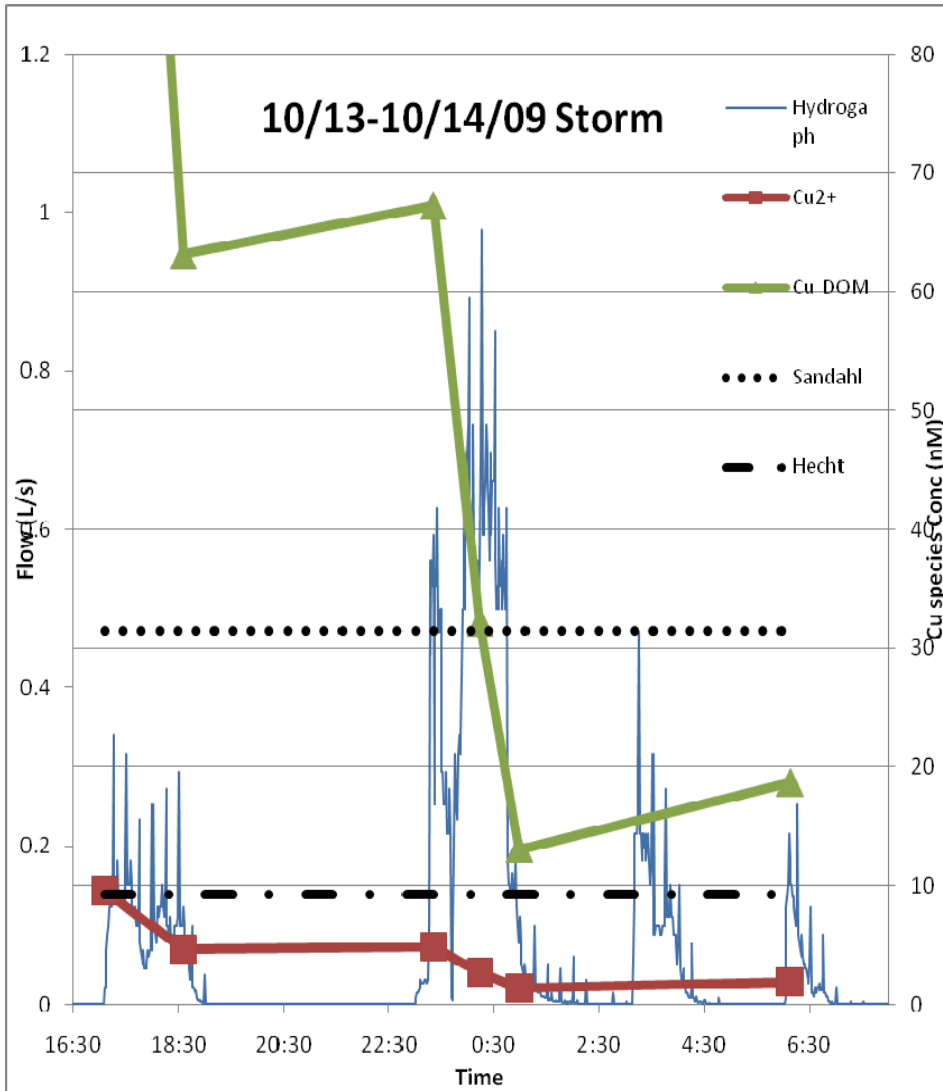


Figure 4.45: Intra-storm free ionic copper and Cu-DOM

The Gaussian DOM model is based on a single type of well-characterized DOM molecule (Suwanee Fulvic Acid) and may not be an accurate representation of DOM in stormwater. Furthermore, the Gaussian distribution of binding site number to binding site strength (as outlined in Section 2.7) may or may not accurately predict copper-DOM binding in these samples. For these reasons, analytically determining copper speciation in stormwater is important. Comparisons of analytically determined and modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations are discussed in the following section.

4.2.6.5 Comparison Chemical Equilibrium Modeling with CLE-ACSV Results

The Gaussian DOM model utilized in the above analysis is a relatively simple organic binding model. For the purposes of comparing model results with analytically determined speciation, two more sophisticated DOM models (the NICA-Donnan model and the Stockholm Humic Model) were utilized in addition to the Gaussian DOM model. Again, stormwater samples were modeled using Visual MINTEQ. For this analysis, modeling was performed at the same conditions as the CLE-ACSV determinations; that is, pH 6.80, and elevated Na and Cl concentrations. Table 4.8 compares the modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations with analytical measurements.

Table 4.8: Comparison of experimentally determined and modeled free ionic copper concentrations

Sample	Measured \log [$\text{Cu}^{2+}_{\text{free}}$] (M)	Gaussian \log [$\text{Cu}^{2+}_{\text{free}}$] (M)	NICA- Donnan \log [$\text{Cu}^{2+}_{\text{free}}$] (M)	SHM \log [$\text{Cu}^{2+}_{\text{free}}$] (M)
Bend Site				
12-29-09	-11.69	-7.93	-10.10	-10.41
03-16-09 ^a	-10.85	-7.59	-9.16	-9.77
I-5 Site				
10-06-08	-7.38	-7.18	-8.96	-9.40
11-02-08	-6.74	-7.40	-9.50	-9.84
11-03-08 ^a	-11.08	-7.47	-9.41	-9.77
11-20-08 ^a	-7.18	-7.34	-9.24	-9.57
Dixon Site				
11-20-08	-12.20	-7.99	-10.31	-10.58
12-01-08	-12.75	-8.14	-10.29	-10.64
02-06-09 ^a	-11.80	-7.87	-9.96	-9.83
02-23-09	-12.62	-7.90	-9.74	-10.17
03-14-09	-12.97	-8.07	-9.93	-10.39
04-12-09	-12.34	-7.80	-9.62	-10.11
05-13-09	-11.11	-7.74	-9.96	-9.13
10-13-09	-11.77	-8.13	-10.57	-10.70
Wemme Site				
11-20-08	-12.60	-8.08	-10.38	-10.67
12-01-08	-12.50	-7.94	-9.81	-10.24
01-06-09 ^a	-11.02	-7.45	-9.15	-9.60
03-11-09	-10.86	-7.64	-10.20	-10.22
03-24-09 ^a	-11.30	-7.87	-9.97	-10.23
05-05-09	-12.27	-7.94	-9.78	-10.18

Note: 2 μM SA Results

Rigorous statistical comparisons between modeled and experimentally determined $\text{Cu}^{2+}_{\text{free}}$ concentrations cannot be made due to the unknown error associated with the models. However, all three DOM models overestimate the $\text{Cu}^{2+}_{\text{free}}$ concentration determined by CLE-ACSV by one to three orders of magnitude. The Gaussian DOM model consistently predicted the highest $\text{Cu}^{2+}_{\text{free}}$ concentrations, while the Stockholm Humic Model predicted the smallest

concentrations of $\text{Cu}^{2+}_{\text{free}}$. In general, results from the NICA-Donnan and Stockholm Humic Model were similar. For the majority of samples the primary copper species were:

$$[\text{Cu} - \text{DOM}] \gg [\text{Cu}^{2+}_{\text{free}}] > [\text{CuCO}_3] \approx [\text{CuOH}^+] \quad (4-1)$$

As discussed above, the Wemme sample collected on 3/24/09 was unique in that $\text{Cu}^{2+}_{\text{free}}$ was the most abundant species in the Gaussian model due to Ca and Mg competing with copper for DOM. Overall, the trend in modeled species concentrations in Equation (4-1) agrees with experimental results.

Despite the fact that modeled $\text{Cu}^{2+}_{\text{free}}$ concentrations overestimate the concentrations determined by CLE-ACSV, general trends in the modeled results reflect those of the analytical determinations. Furthermore, the chemical equilibrium models can be viewed as a conservative estimate of the $\text{Cu}^{2+}_{\text{free}}$ concentrations. Even these conservative estimates of the $\text{Cu}^{2+}_{\text{free}}$ concentrations were substantially less than the 2 $\mu\text{g/L}$ toxicity threshold. The fact that modeling copper speciation requires substantially less time and effort than analytically determining $\text{Cu}^{2+}_{\text{free}}$ concentrations makes this option appealing. With a few relatively simple analytical measurements ($\text{Cu}^{2+}_{\text{diss}}$, dissolved organic carbon, alkalinity, hardness, and ionic strength), a reasonable estimate of the aqueous speciation of copper can be made using readily available models. The fact that these estimates (using chemical equilibrium models incorporating generic DOM models) are comparable to analytically determined values is a promising sign that the analytical determinations are correct.

As stated above, the DOM models utilized in this work were derived using parameters specific to a single organic matter source (Suwannee River Fulvic Acid). It is highly likely that the organics in stormwater are different. More accurate predictions of $\text{Cu}^{2+}_{\text{free}}$ concentrations could be obtained through the development of DOM parameters reflective of stormwater DOM. This may include an increase in the number of copper-DOM sites, or in the competitive strength of copper for DOM sites. To determine an accurate fit to all free cation concentrations in stormwater a more in-depth investigation into the speciation of cations in stormwater would be necessary. The use of DOM models for stormwater will likely be limited by the fact that an 'average' DOM molecule may not exist that accurately represents the heterogeneous nature of highway stormwater runoff. Based on the CLE-ACSV analysis, the variation in ligand concentrations and stability constants at the four sites examined in this study is significant. In the meantime, one of the available humic binding models (preferably the NICA-Donnan or Stockholm Humic Model, as they more closely predicted measured values) could be used as a conservative estimate of $\text{Cu}^{2+}_{\text{free}}$ concentrations in stormwater. More work is needed to determine if available models are appropriate for predicting copper speciation in stormwater and natural receiving waters. With regulatory agencies moving toward the use of Biotic Ligand models that account for humic binding, better characterization of the nature and characteristics of the organic matter present in stormwater and receiving waters will be necessary.

5.0 CONCLUSIONS

The objectives of this study were 1) to identify the effects of site location, storm hydrology, and water quality parameters on the concentration of $\text{Cu}^{2+}_{\text{diss}}$ in Oregon highway runoff; 2) to establish an analytical technique suitable for the determination of copper speciation in highway stormwater runoff; 3) to compare analytically determined $\text{Cu}^{2+}_{\text{free}}$ concentrations in highway stormwater runoff with modeled concentrations; and 4) to develop a qualitative understanding of where and when copper toxicity has the most potential to be problematic for receiving waters. The following conclusions were reached during the completion of these objectives:

- In this study, stormwater runoff from an urban site characterized by high annual average daily traffic (AADT) (the I-5 site) had consistently higher event mean concentrations (EMCs) of measured $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$ than three non-urban sites with lower AADT. The separate effects of urban site location and AADT could not be extracted in this study. In terms of practical implications, the distinction between the effects is often immaterial – urban sites are characterized by high traffic densities and vice versa. High AADT/urban highways show the most potential for producing runoff that would exert copper toxicity
- There was little evidence to suggest significant differences in $\text{Cu}^{2+}_{\text{diss}}$ in stormwater measured at the other three sites, which varied in terms of eco-region and AADT.
- First flush samples displayed consistently higher concentrations of both $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. This agrees with many previous works. The first flush of a storm shows more potential for copper toxicity than runoff further along in the storm's progression.
- There was insufficient evidence to support any effects of antecedent dry period (ADP), total rainfall, rainfall duration, or average rainfall intensity on $\text{Cu}^{2+}_{\text{diss}}$ concentrations in composite samples. There was also no significant effect of ADP on $\text{Cu}^{2+}_{\text{diss}}$ in first flush samples from the Dixon Outfall site. It is possible that if more samples were collected, significant correlations with these hydrologic parameters would be determined.
- In a multiple linear regression (MLR) model, the water quality parameters which demonstrated the greatest ability to predict $\text{Cu}^{2+}_{\text{diss}}$ were dissolved organic carbon (DOC) and alkalinity, both having positive associations with $\text{Cu}^{2+}_{\text{diss}}$. The model also included less significant terms accounting for negative correlations with pH and hardness. The primary value of this model is in determining important water quality predictors of copper, not in determining a quantitative equation, which would likely be inaccurate and highly location-specific.

- In an MLR model to predict $\text{Cu}^{2+}_{\text{tot}}$ concentrations in highway stormwater runoff, the most important parameters were determined to be DOC and total suspended solids (TSS), both having positive associations with $\text{Cu}^{2+}_{\text{tot}}$. Again, developing a quantitative predictive model could give the false impression that copper concentrations could actually be calculated knowing other water quality parameters.
- A modified CLE-ACSV technique utilizing salicylaldoxime (SA) as an added ligand can be used to determine the speciation of copper in highway stormwater runoff. Ambient stormwater pH in this study (6.80) lowered the sensitivity of the method; the addition of an electrolyte to compensate for this effect was necessary. Great care must be taken in the selection of SA concentrations to test stormwater, as the Cu-ligand stability constants can vary widely within and between sites. Furthermore, the method is difficult to implement in the dirtiest samples with high $\text{Cu}^{2+}_{\text{diss}}$ concentrations and surfactants or other compounds that may foul the mercury drop electrode.
- Analytical results from composite stormwater samples suggest that dissolved copper in highway stormwater runoff is largely complexed by organic matter (typically > 99.9%) and that very little of the copper in stormwater is bioavailable; the concentrations of $\text{Cu}^{2+}_{\text{free}}$ were generally several orders of magnitudes below levels found to inhibit olfaction in ESA-listed fish species.
- Elevated $\text{Cu}^{2+}_{\text{diss}}$ levels proved to be the greatest indicator of high $\text{Cu}^{2+}_{\text{free}}$ concentrations. Urban sites with AADT and first flush samples characterized by elevated concentrations of $\text{Cu}^{2+}_{\text{diss}}$ are of the greatest concern with respect to elevated free ionic copper concentrations.
- Hardness, as a measure of major divalent cations, is also a good indicator of $\text{Cu}^{2+}_{\text{free}}$ concentrations. Calcium and magnesium competition with copper for ligand sites drives copper into its free ionic form. Hardness-related issues with $\text{Cu}^{2+}_{\text{free}}$ are of greatest concern after the application of road salts for anti-icing and de-icing of highways. This was revealed through examination of four of the Wemme composite samples, showing much higher concentrations of hardness compared with other Wemme composite samples. Consideration must be given to these effects to mitigate potential problems with $\text{Cu}^{2+}_{\text{free}}$ concentrations in receiving water bodies.
- The overall effect of hardness on toxicity in stormwater is complex. Divalent cations compete with $\text{Cu}^{2+}_{\text{diss}}$ both for adsorption sites on DOM (increasing free $\text{Cu}^{2+}_{\text{free}}$), but also compete with $\text{Cu}^{2+}_{\text{free}}$ for biotic ligand sites on aquatic organisms (reducing toxicity).
- Organic ligand and $\text{Cu}^{2+}_{\text{diss}}$ concentrations are positively correlated with DOC concentrations. $\text{Cu}^{2+}_{\text{free}}$ levels are also positively correlated with DOC concentrations. Likely there are co-variance issues, but overall, DOC is not a strong predictor of $\text{Cu}^{2+}_{\text{free}}$ concentrations.

- Cu-Ligand conditional stability constants vary widely within and across sampling sites. Highly urbanized sites, such as the I-5 site, generally had weaker ligands when compared with less-urbanized sites with mixed sources of organic material. Petroleum and chemical-based organics likely dominate urbanized sites and appear to have lower copper complexation capacities.
- Available DOM models in Visual MINTEQ overestimate $\text{Cu}^{2+}_{\text{free}}$ concentrations when compared to analytically determined $\text{Cu}^{2+}_{\text{free}}$ concentrations. The Stockholm and NICA-Donnan models provide the best estimates for $\text{Cu}^{2+}_{\text{free}}$ concentrations, but may exceed analytical concentrations by over an order of magnitude. This is likely due to the poor representation of highway stormwater runoff organic matter in these models. Despite these facts, the results from chemical equilibrium models followed similar trends as the analytical speciation results and are likely a reasonably conservative estimate of copper speciation in highway stormwater runoff.

5.1 FUTURE WORK

There are several key areas for future investigative work stemming from this study.

Determining $\text{Cu}^{2+}_{\text{free}}$ concentrations in water bodies requires significant time, effort, skill, and analytical equipment. For this reason, routinely measuring $\text{Cu}^{2+}_{\text{free}}$ concentrations for regulatory purposes is not advisable. Although correlations were observed between bulk water quality parameters (dissolved copper, hardness, DOC, and alkalinity) and $\text{Cu}^{2+}_{\text{free}}$ concentrations, these measurements in isolation do not lend themselves to robust predictive capabilities. It is suggested that copper toxicity levels be determined for species of interest (e.g., Coho salmon) through establishing $\text{Cu}^{2+}_{\text{diss}}$ concentrations at specific DOC and hardness levels that result in high risk for toxicity. In order to accomplish this, a replication of the Sandahl, et al. (2007) and McIntyre, et al. (2008) studies with the addition of copper speciation techniques and characterization of natural organic matter would more robustly quantify toxic $\text{Cu}^{2+}_{\text{diss}}$ concentrations for Coho salmon under different water quality conditions. This information could be incorporated into a Biotic Ligand Model or similar framework and used by regulators to determine the danger of copper levels to ESA-listed fish.

The relationship between DOC concentrations, types of DOC, and $\text{Cu}^{2+}_{\text{free}}$ concentrations in highway stormwater runoff is unknown. Future work should attempt to more fully characterize DOC and copper speciation at a few selected sites in order to determine the effects of different types of DOC on $\text{Cu}^{2+}_{\text{free}}$ concentrations. Sites with a single dominant organic source (highly urbanized zones) could be contrasted with sites that have a variety of organic sources. This information could be used by regulators to establish ‘high risk’ locations to receive mitigation. Along these lines, characterizing DOM from streams inhabited by ESA-listed salmon species is of paramount importance. An effort to both characterize the DOM and measure $\text{Cu}^{2+}_{\text{free}}$ in a single receiving water may provide information on the role of specific functional groups in binding copper in natural waters.

There is also potential work in analyzing the effects of highway runoff in receiving waters. Highway runoff comprises only a fraction of the total volume of a receiving

water. However, this fraction may be small or large, depending on a specific site's surrounding paved area, location within a watershed, the time of the year, etc. A study investigating different dilutions of highway runoff with natural waters and/or the $\text{Cu}^{2+}_{\text{free}}$ concentrations in receiving bodies as a function of distance from the stormwater source would be essential in determining whether or not stormwater is a potential threat to ESA-listed species. The extent to which copper bound with organics in stormwater will repartition once the stormwater mixes with natural waters needs investigation. Furthermore, the capacity of different natural waters to complex copper and the kinetics of those processes are not well understood.

The very nature of stormwater studies makes strong conclusions difficult to reach. Highway sites have different traffic levels, are located in different eco-regions, are surrounded by a variety of land uses, and even experience storms of varying magnitude and nature at different points in time. Therefore, it is nearly impossible to isolate the effect of a single variable in a stormwater study. Future work involving stormwater should include more extensive sampling efforts focused on examining a single variable. For example, the separate effects of AADT and eco-region could be examined at a large number of different sites, all located within the same eco-region. Another possible study would involve isolating the individual effects of AADT and urban sites. This could be researched by selecting a number of sampling sites with various AADTs which are all located within the same urban area. Such a study would also eliminate some of the inherent variability in analyzing samples arising from different storms. Any future stormwater study should be long term – over the course of years. This would help determine if any observed trends are only a function of seasonality.

Finally, an analytical model that accurately determines $\text{Cu}^{2+}_{\text{free}}$ concentrations in stormwater is currently unavailable. An investigation into common DOC characteristics and the speciation of cations in a stormwater would go a long way in aiding the establishment of an accurate copper speciation model. This model would be a powerful tool for regulators to determine the speciation of copper in stormwater. As regulations move towards the use of Biotic Ligand Models to predict toxicity of metals in surface waters, it will be important to insure that the humic binding models accurately represent the varied sources of organic matter present in stormwater and natural waters. The framework for these models exists, but continued characterization of additional organic matter types is necessary, to provide inputs to the existing models.

5.2 SIGNIFICANCE

In addressing the significance of this project for regulatory agencies, several important topics emerge. These include delineation of the appropriate conditions for the application of the analytical technique, use of the data from this study to identify (high risk) sites for future study, a discussion of the limitations of available chemical equilibrium models, the influence of de-icing salts, and a summary of suggestions for future monitoring of copper in stormwater.

Routine measurement of $\text{Cu}^{2+}_{\text{free}}$ concentrations in waters of interest (stormwater samples or receiving bodies) by regulatory organizations is not the appropriate use of the CLE-ACSV technique. This technique requires specialized training, an extensive time

commitment to fully characterize a sample, and a high level knowledge of the meaning of the results. The modified CLE-ACSV technique has been shown to be instrumental in characterizing composite highway stormwater runoff samples. However, the method has shown difficulties in characterizing samples with extremely high $\text{Cu}^{2+}_{\text{diss}}$ concentrations (as high or higher than those reported from the I-5 site) or a high concentration of surfactants (potentially any stormwater sample, especially first flush samples). All these problematic issues cause CLE-ACSV to be cumbersome for regularly monitoring water quality. Utilization of CLE-ACSV should remain primarily a research tool.

Potentially lost amidst the correlations and analyses developed in the preceding sections is a simple but important fact: salmonids don't live in stormwater. Although examining copper speciation in stormwater is useful and does provide an idea of when and where toxicity in receiving waters might be a problem, failing to study the actual receiving waters would be a great oversight. However, in examining both the statistics on $\text{Cu}^{2+}_{\text{diss}}$ and the speciation for $\text{Cu}^{2+}_{\text{free}}$, it was shown that highway runoff arising from the first flush of a storm, as well as highway runoff from urban/high-traffic areas with little to no natural organic sources, has the most potential to adversely affect ESA-listed species. Additionally, the first flush effect is amplified in small catchments and highly impervious watersheds. It follows then, that treating the first flush of a storm in an urban area would have the greatest effect on reducing the potential toxicity to aquatic species. Therefore, the most effective best management practices (BMPs) for treating highway runoff should focus on those sites and conditions. It is important to recognize, however, that in this study it was found that the vast majority of $\text{Cu}^{2+}_{\text{diss}}$ in highway stormwater runoff samples was bound with organic matter and likely not bioavailable.

Hardness was shown to have a strong positive correlation with free Cu^{2+} . This is of particular interest because the very high concentrations of hardness, which significantly affect copper's speciation, likely arise from adding de-icing salts to the road, specifically magnesium chloride. However, as noted in Chapter 2, calcium and magnesium have also shown a significant effect in reducing copper toxicity to fish. This effect is primarily due to their competition with $\text{Cu}^{2+}_{\text{free}}$ for biotic ligand sites on the fish. Therefore, the overall effect of hardness on toxicity in the presence of organic ligands is still in question. Properly characterizing this effect in receiving waters would be important prior to making a determination about how the application of magnesium chloride to Oregon highways affect copper toxicity in aquatic species.

The comparison between modeled and analytically determined $\text{Cu}^{2+}_{\text{free}}$ concentrations is important. These results show that the models utilized in this study are not reflective of actual DOM in Oregon highway stormwater runoff. Model predictions would likely be improved with improved characterization of the organic matter present in highway stormwater runoff. However, existing models may still be reasonably accurate for regulatory purposes in Oregon highway stormwater runoff with low $\text{Cu}^{2+}_{\text{diss}}$ concentrations (non-urbanized sites) and situations where the toxicity levels exceed predicted $\text{Cu}^{2+}_{\text{free}}$ concentrations by multiple orders of magnitude (as was the case in this study for non-I-5 sites/non-first flush samples). All equilibrium model results for $\text{Cu}^{2+}_{\text{free}}$ concentrations appear to provide conservative estimates of $\text{Cu}^{2+}_{\text{free}}$ concentrations when applied to Oregon highway stormwater runoff.

The work reported here builds on an already substantial body of knowledge involving the presence of heavy metals in stormwater, aquatic speciation of heavy metals, and heavy metal toxicity to aquatic organisms. This study is the first to analytically determine copper speciation in stormwater. As such, the work provides unique insight into the risks associated with copper in highway stormwater runoff. Although the results reported here indicate that copper is largely bound with organics in stormwater, many questions remain regarding the nature of those organics, what happens to the copper once the stormwater is discharged to surface waters, how best to mitigate copper in stormwater, and how to best incorporate this information into a regulatory framework. Biotic Ligand Models that are currently being used to regulate heavy metals in surface waters would benefit from continued efforts to analytically verify model outputs and efforts to more fully characterize the organic ligands present in stormwater and natural waters. The methods developed as part of this study will be instrumental in accomplishing those objectives.

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APPENDICES

A.1 QUALITY ASSURANCE/QUALITY CONTROL

A variety of steps were taken in this study to check the quality of the data being obtained, including measuring replicate samples, testing field and method blanks, and analyzing spiked samples. The results for these measurements are shown in Table A.1 through Table A.4. Blanks were used to estimate contamination from field and lab practices and procedures. Most analytes for the field blanks (shown in Table A.1 and Table A.2) measured below detection – either below the detection limit for the instrument or below the least concentrated standard used to generate a calibration curve. Unusually high concentrations of Zn were measured in the Dixon 2/23/09 and 3/14/09 field blanks, while the Dixon 4/12/09 field blank showed a relatively high Na concentration. The high NO₃ concentration in the 10/13/09 field blank is likely due to residue from cleaning out the Teflon intake tubing with nitric acid, though the tube was rinsed with 2 L of DDI after the acid wash. This residue was likely further diminished by intaking volume calibration samples at the site, which occurred after taking the field blank. The measured NO₃ found in the method blank was likely due to the filters being acidified in nitric acid prior to use, though each filter was rinsed with 250 mL of DDI prior to use. Low levels of copper were found in the 12/1/08 and 3/14/09 field blanks.

Table A.1: Cation and DOC blank measurements

Sample	Ca	Fe	K	Mg	Na	Cd	Cu	Ni	Pb	Zn	DOC
	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppm
Dixon 12/1/08 FB	0.16	bdl	bdl	bdl	0.72	.009	1.23	bdl	bdl	2.31	0.23
Dixon 2/23/09 FB	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1.99	14.5	0.26
Dixon 3/14/09 FB	bdl	bdl	0.13	bdl	0.51	bdl	1.43	1.62	bdl	13.6	0.34
Dixon 4/12/09 FB	0.08	bdl	bdl	bdl	2.05	bdl	bdl	bdl	bdl	5.57	0.20
Dixon 10/13/09 FB	bdl	bdl	bdl	bdl	0.11	bdl	bdl	bdl	bdl	bdl	bdl
Dixon 10/13/09 MB	bdl	bdl	bdl	bdl	0.083	bdl	bdl	bdl	bdl	bdl	0.32

Table A.2: Anion blank measurements

Sample	Cl	NO ₂	NO ₃	PO ₄	SO ₄
	ppm	ppm	ppm	ppm	ppm
Dixon 10/13/09 FB	0.23	bdl	1.85	bdl	bdl
Dixon 10/13/09 MB	bdl	bdl	0.53	bdl	0.083

For some samples, a synthetic spike from our lab was added in a 4:1 sample:spike ratio. The lab results from analyzing matrix spikes in samples are shown in. This check was meant to analyze how effective a method is at quantifying an analyte, by comparing analytically measured concentrations against predicted concentrations. The percent differences displayed in the table were calculated according to Equation shown below. Measurements marked ‘N/A’ indicate that the sample measurement for that analyte was below detection, which would inherently lead to less accurate results. Relatively high variation between measured and expected results was found in some spiked samples for

K, Na, Ni, and Pb. Expected and measured values for Cu were always in good agreement in the spiked samples.

$$\%Diff = \frac{(Predicted\ Conc. - Measured\ Conc.)}{Measured\ Conc.} \times 100 \quad (A-1)$$

Table A.3: Matrix spike percent differences

Sample	Ca	Fe	K	Mg	Na	Cd	Cu	Ni	Pb	Zn
Dixon 2/6/09 Comp	+3.8	N/A	N/A	+4.1	+9.8	-1.5	-1.6	+2.0	+0.8	-1.8
Dixon 3/14/09 Comp	+5.5	N/A	-3.2	+6.0	+2.0	N/A	+0.1	N/A	-30.4	-2.8
Dixon 10/13/09 Comp	-9.6	N/A	+18.2	+1.7	+36.4	N/A	+2.1	N/A	N/A	-1.3
Wemme 5/5/09 Comp	-12.8	N/A	-32.8	+8.9	-31.8	N/A	-0.7	+47.0	+13.1	-0.6

Table A.4 below shows the results from examining sample replicates. Samples were measured in triplicate for most analyses in an attempt to quantify the consistency of both lab practices and the analytical method. The Coefficient of Variation (COV) for each sample was measured as the sample standard deviation divided by the sample mean and represents the relative variability within a sample. A high COV indicates poor consistency within a sample measurement. A COV of 0.20 (or 20% variability) was chosen as a cutoff point for samples exhibiting high variability. Most samples were well below this criterion, depending on the analyte. The data from these samples was recorded, but flagged. K, Ni, and Pb consistently showed high variation in sample replicates. This fact may also contribute to the poor spike results for those analytes discussed earlier. Ni, Pb, NO₂ and PO₄ frequently measured below detection limits. Fe in many samples was not accurately quantified due to it being below the detection limit for ICP-AES and unable to be quantified on ICP-MS. Of particular importance to this study is the low variation exhibited in measurements for Cu and DOC.

Table A.4: Coefficient of variation analysis and sample measurement notes

Analyte	COV > 0.20	Other Notes
pH	0/43	COV not meaningful on log scale
Conductivity	4/43	
Alkalinity	1/43	
TSS	3/43	
DOC	1/71	
Ca	1/85	6 samples above calibration range
Fe	2/78	21 samples not accurately measured
K	13/90	1 sample below detection
Mg	1/83	8 samples above calibration range
Na	5/91	
Cu	0/114	
Cd	0/40	74 samples below detection
Ni	16/97	
Pb	22/82	32 samples below detection
Zn	1/95	19 samples above calibration range
Cl	2/48	
NO ₂	1/9	37 samples below detection
NO ₃	1/48	
PO ₄	3/6	40 samples below detection
SO ₄	1/48	

A.2 DIXON OUTFALL STORM DATA

This appendix is a collection of the summarized data for Storms collected at Dixon Outfall. The data includes measured values data recorded by the autosampler. The data is presented as hyetographs and their corresponding stormwater hydrograph. Also displayed on the graphs are the points in the storm where samples were taken. Samples taken throughout the storm but only used in creating a composite for the storm are referred to on the graphs as “Taken Samples”; while samples that were measured for DOC and trace metals, at a minimum, are referred to as “Measured Samples”.

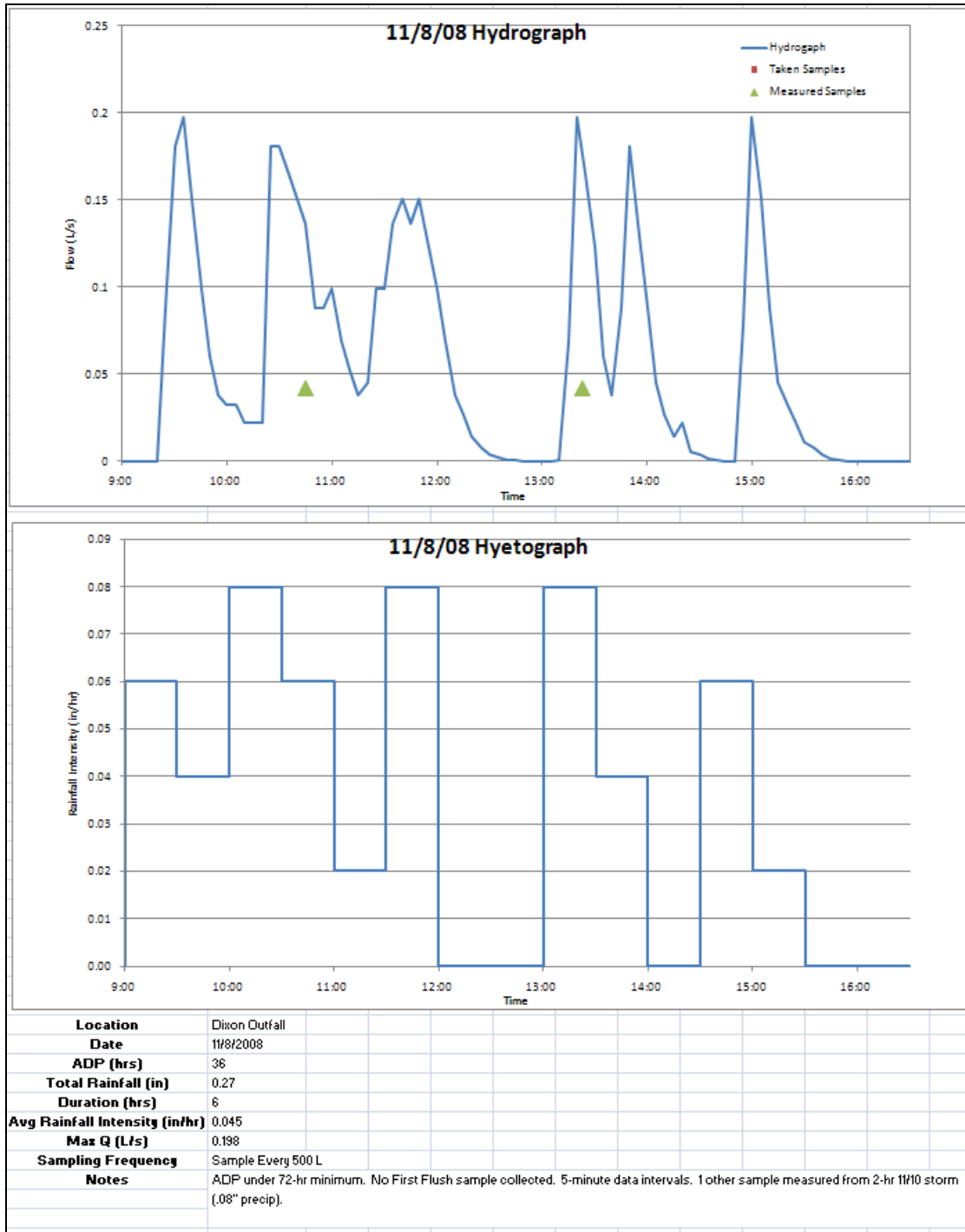


Figure A.1: Dixon Outfall 11/8/08 storm data

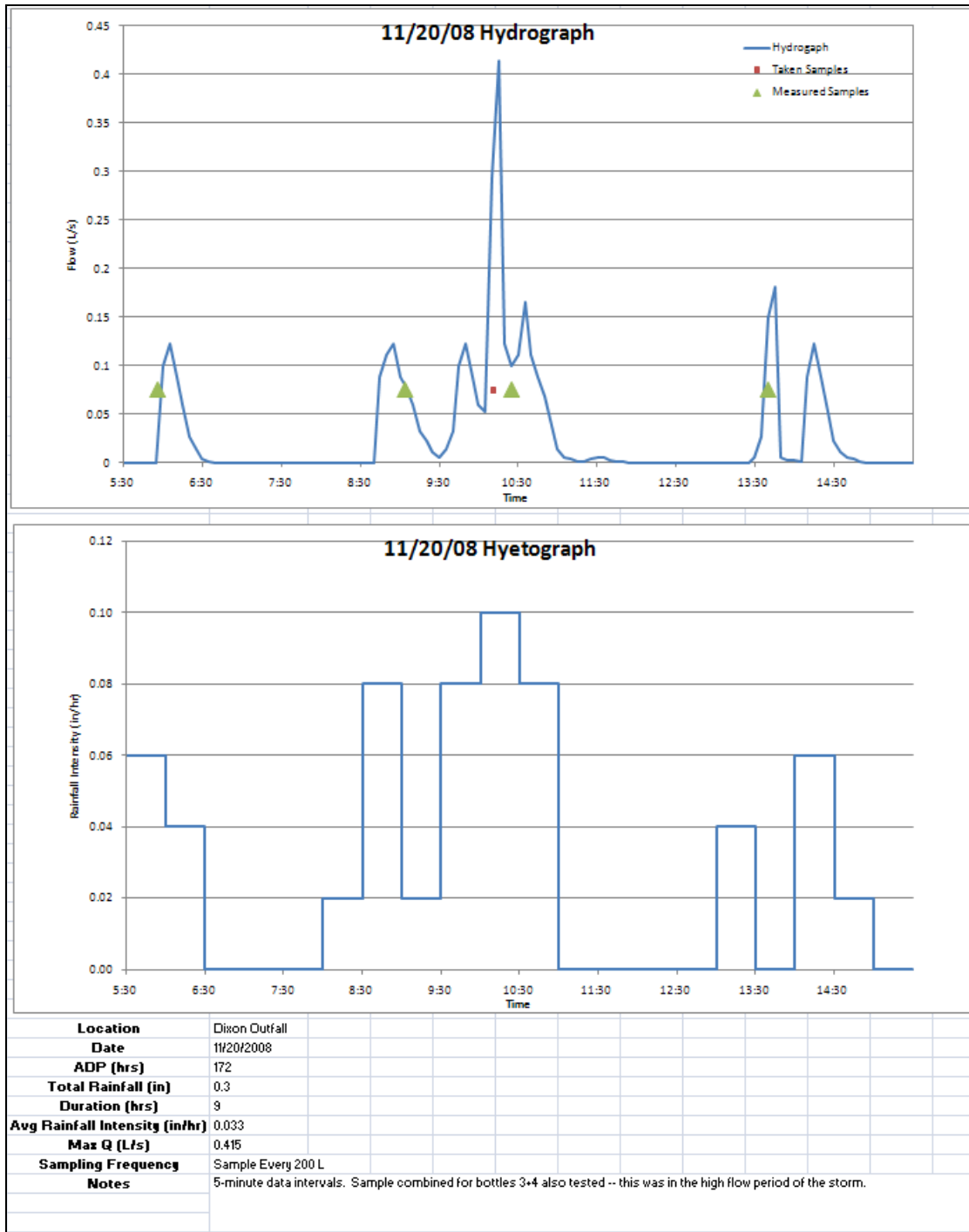


Figure A.2: Dixon Outfall 11/20/08 storm data

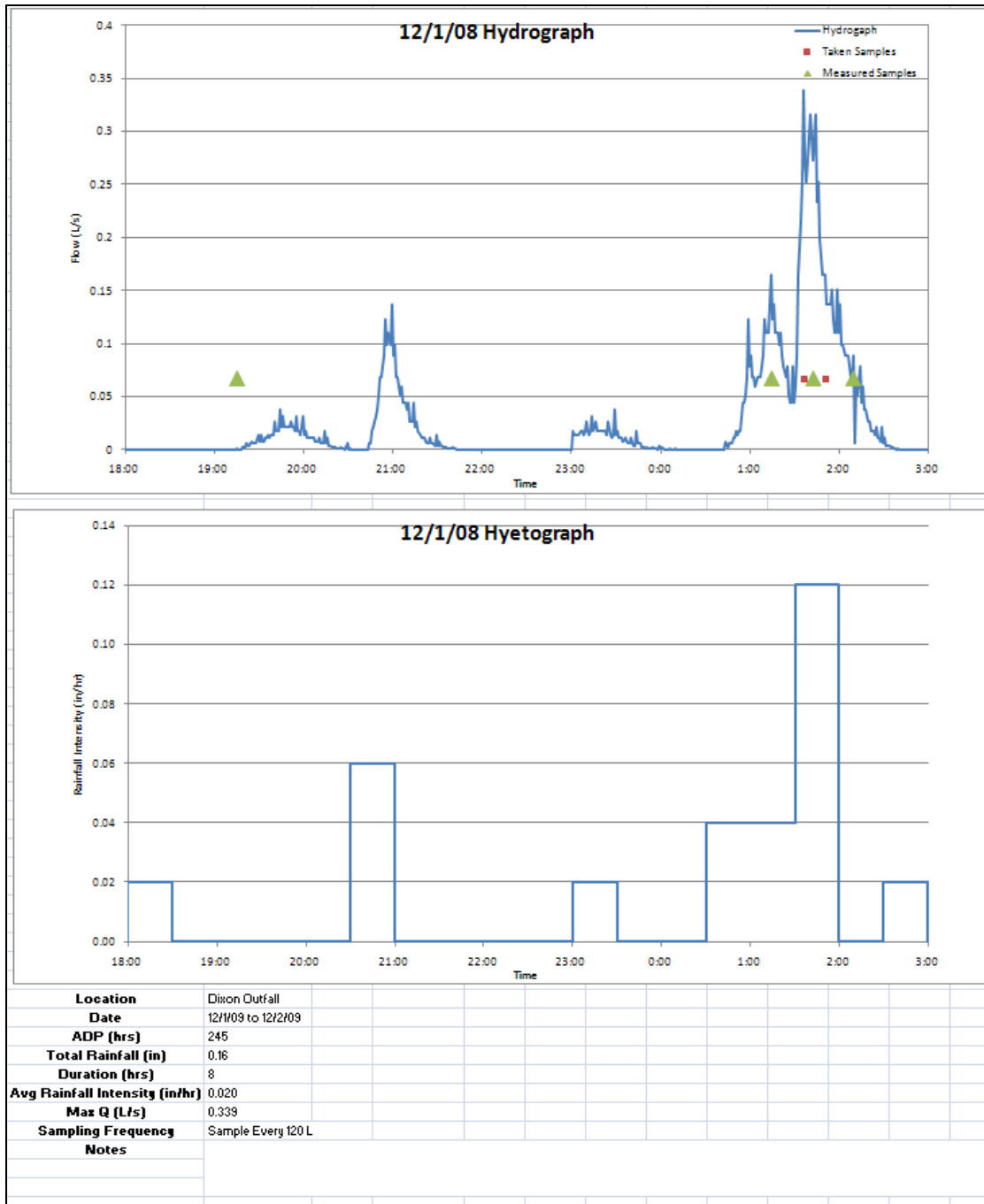


Figure A.3: Dixon Outfall 12/1/08 storm data

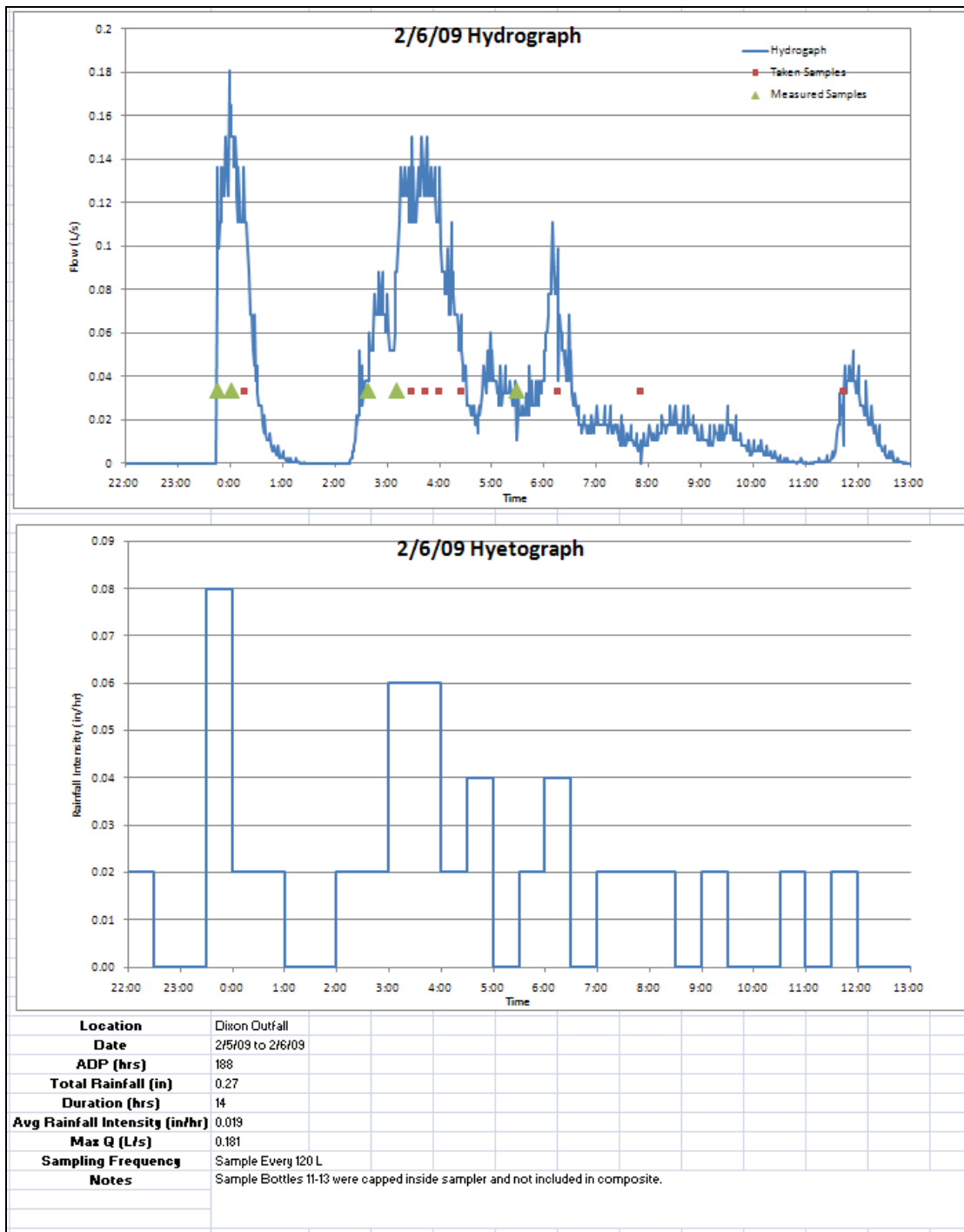


Figure A.4: Dixon Outfall 2/6/09 storm data

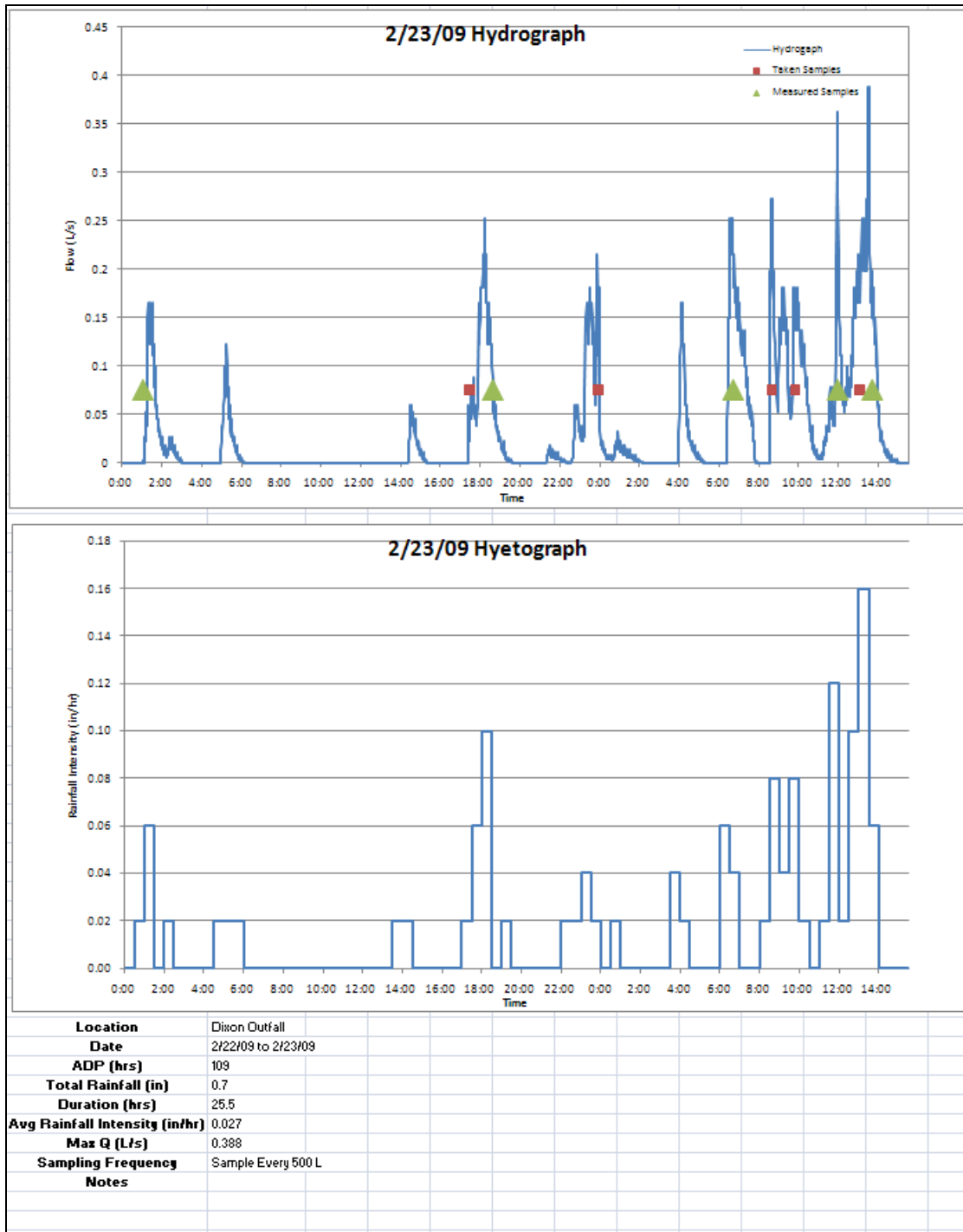


Figure A.5: Dixon Outfall 2/23/09 storm data

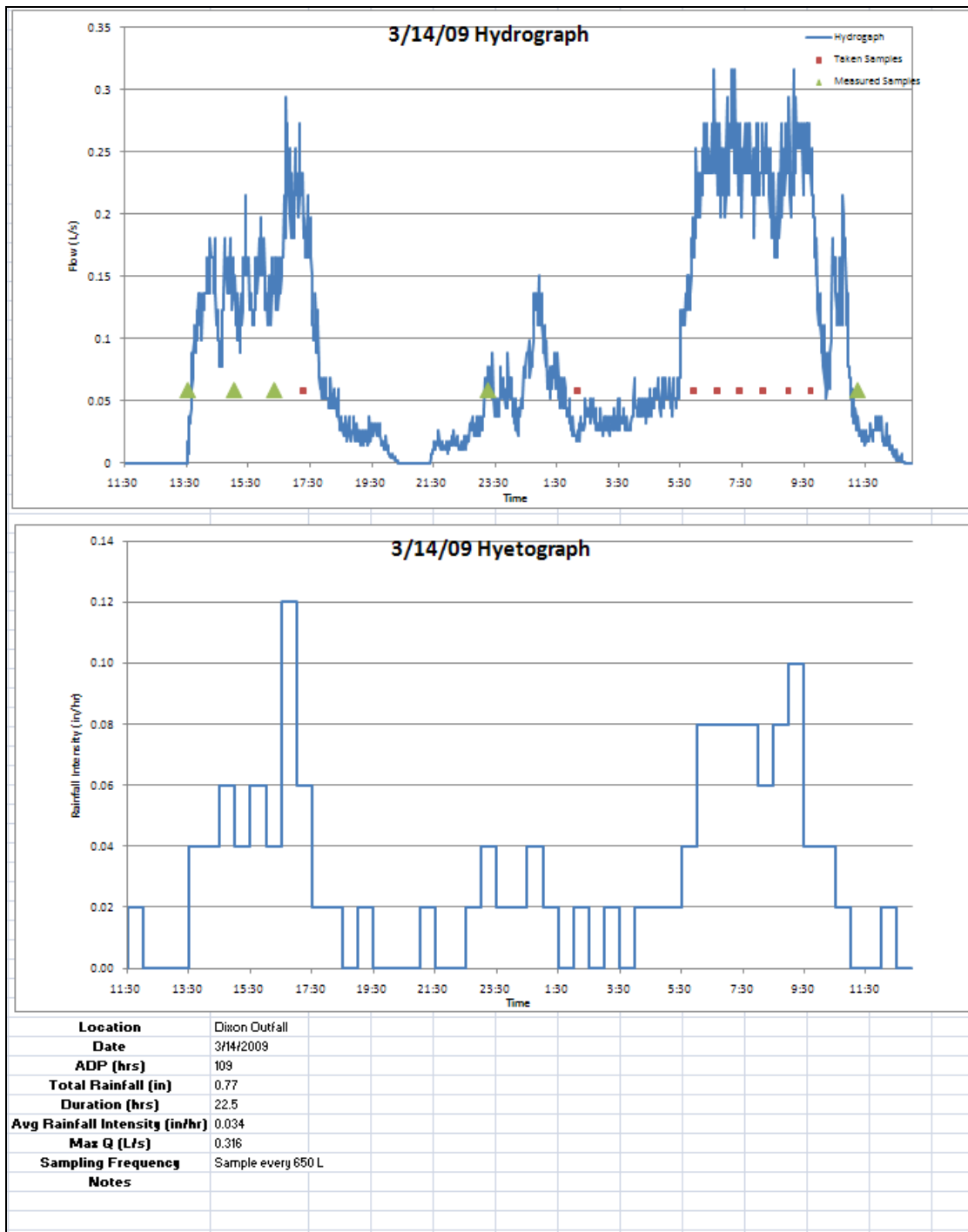


Figure A.6: Dixon Outfall 3/14/09 storm data

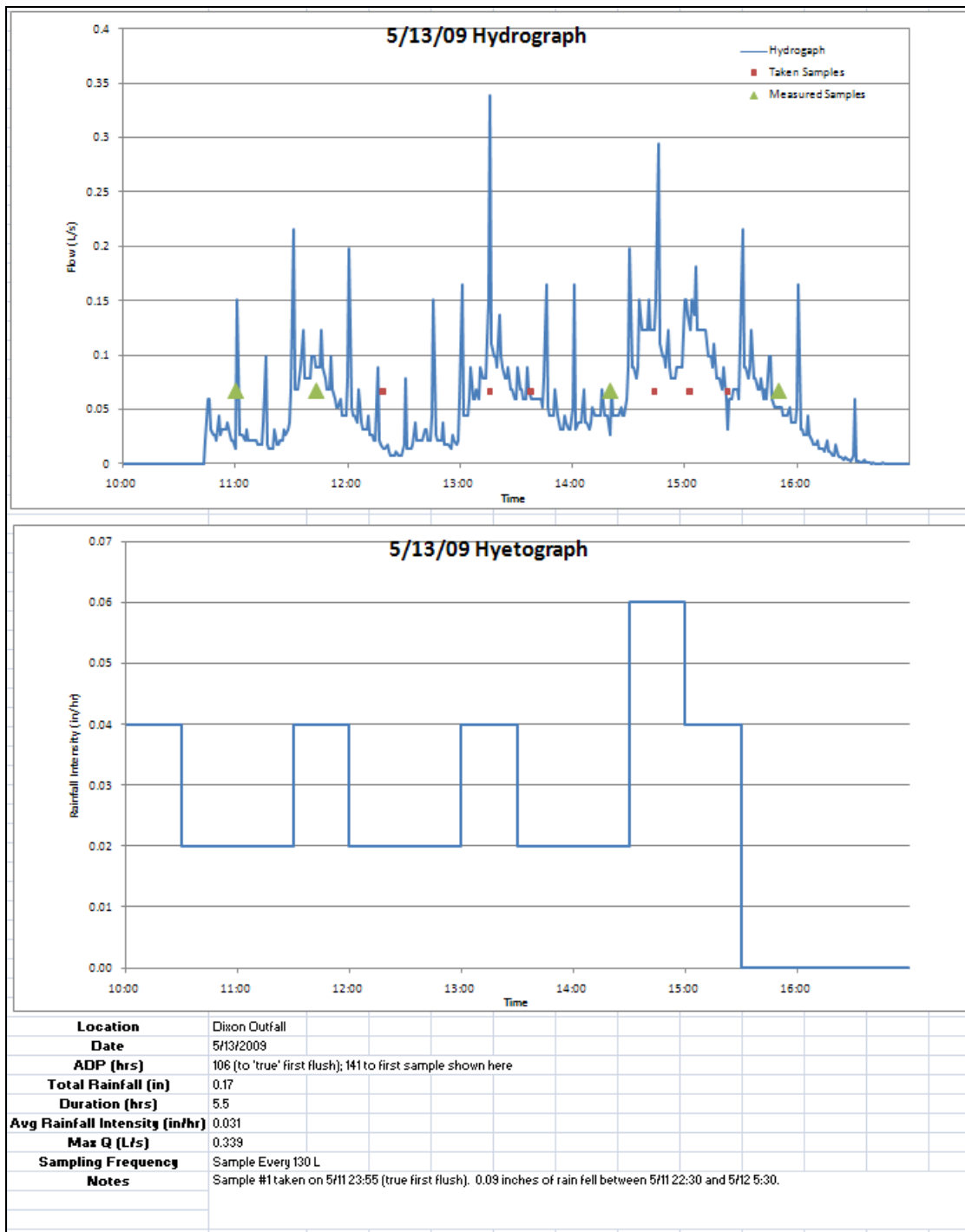


Figure A.8: Dixon Outfall 5/13/09 storm data

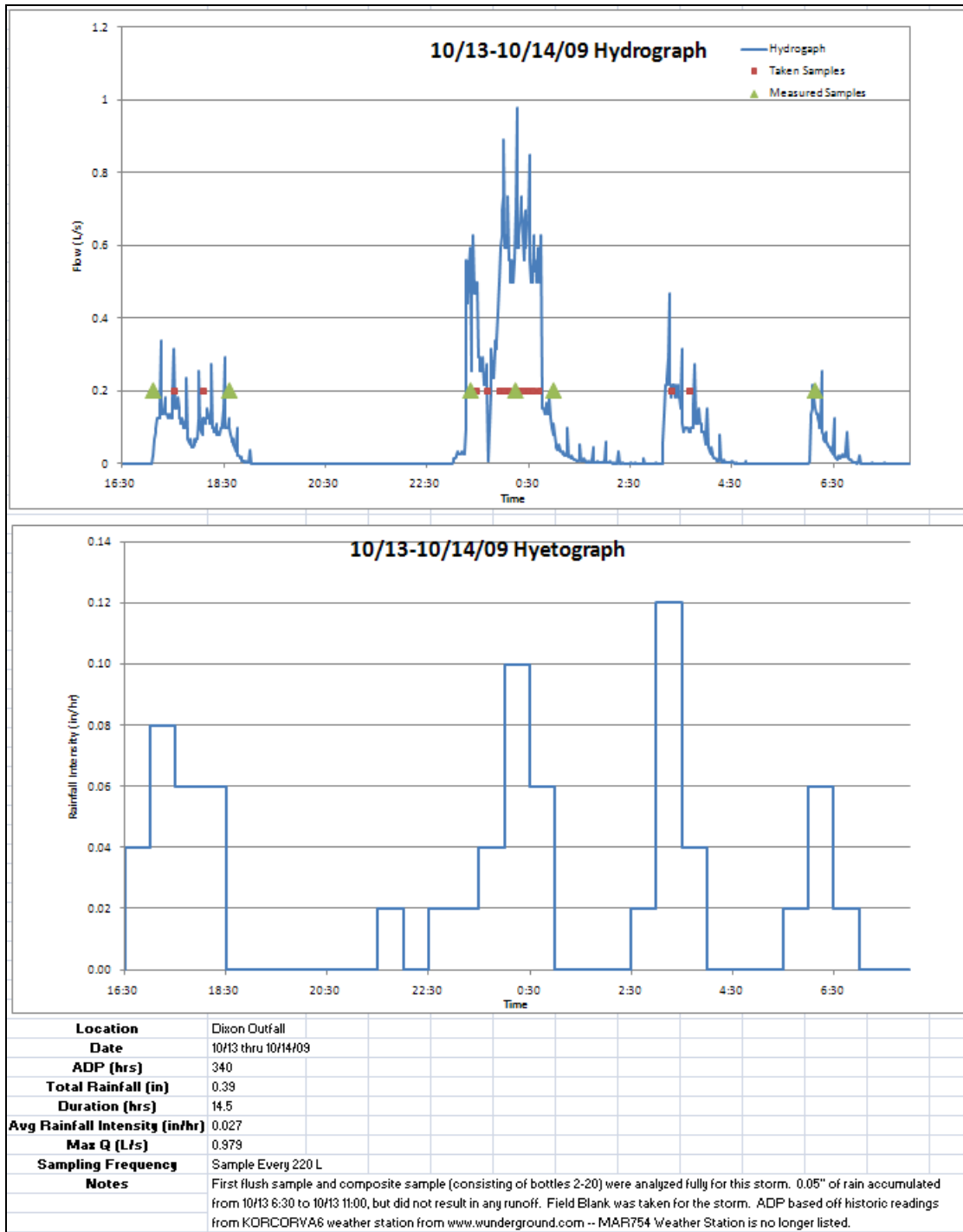


Figure A.9: Dixon Outfall 10/13-10/14/09 storm data

A.3 COMPILED STORMWATER DATA

The measured concentrations from the stormwater samples are presented in this appendix. For easier presentation of the data, the original spreadsheet has been broken down into three categories: Herrera samples, Dixon Outfall composite and first flush samples, and Dixon Outfall grab and flow-weighted samples. Furthermore, each of these subsets is broken into figures: measurement of general water quality parameters and cations, and measurements of anions and hydrologic parameters. Gray rows indicate total samples. Lab measurements from the study by Herrera Environmental Consultants are presented in parentheses where applicable.

Sample	Tot or Diss	pH	Conductivity µS/cm	Salinity psu	Alkalinity mg/L as CaCO ₃	Hardness mg/L as CaCO ₃	TSS mg/L	DOC mg/L	Ca ppm	Cd ppb	Cu ppb	Fe ppm	K ppm	Mg ppm	Na ppm	Ni ppb	Pb ppb	Zn ppb
Bend 12/29/08	Total				36.17	36.17	240.7 (30)	5.16 (3.6)	5.44	0.12 (bdl)	25.75 (38.4)	1.69	0.51	5.97	1.18	8.5	27.6 (15.3)	149 (180)
Bend 12/29/08	Dissolved				27.30	27.30	240.7 (30)	5.16 (3.6)	2.72	0.08 (bdl)	5.21 (5.3)		0.48	4.88	1.17	1.15	bdl (<.001)	28.7 (31)
Bend 3/16/09	Total				70.66	70.66	85.8 (10)	5.8 (4.6)	4.4	bdl (bdl)	21.8 (8.3)	0.44	0.77	14.49	1.49	8.4	8.52 (5.3)	149.8 (88.4)
Bend 3/16/09	Dissolved				70.66	70.66	85.8 (10)	5.8 (4.6)	4.27	bdl (bdl)	8.95 (6.4)	0.24	0.74	15.1	1.6	4.95	0.42 (3.8)	63.5 (75.9)
I-5 3/17/08	Total				52.26	52.26	89.3 (40)	9.97	14.1	0.739 (bdl)	37.9 (36.5)	0.889	3.79	4.14	5.88	2.84	16.8 (14.8)	354 (173)
I-5 3/17/08	Dissolved				43.4 (33.2)	43.4 (33.2)	89.3 (40)	9.97 (3.05)	11.6	0.92 (bdl)	13.2 (6.04)	<0.05	0.956	3.51	5.14	1.35	0.333 (bdl)	193 (37.4)
I-5 10/6/08 #1	Total				31.85	31.85	23.1 (32)	7 (6.6)	9.67	0.37 (bdl)	40.9 (37.4)	0.531	1.56	1.87	3.12	2.1	11.0 (9.17)	105.8 (95.5)
I-5 10/6/08 #1	Dissolved				30.85 (32)	30.85 (32)	23.1 (32)	7 (6.6)	9.42	0.15 (bdl)	22.7 (89)	<0.05	1.49	1.78	2.66	1.19	0.16 (bdl)	43.8 (45)
I-5 10/6/08 #2	Total				30.87	30.87	27.8 (32)	7.07 (8.6)	9.37	0.43 (bdl)	47.7 (37.4)	0.53	1.537	1.815	2.54	1.93	10.78 (9.17)	802.3 (95.9)
I-5 10/6/08 #2	Dissolved				20.175	20.175	27.8 (32)	7.07 (8.6)	6.15	0.15 (bdl)	28.8 (19)	<0.05	0.61	1.03	1.02	1.02	0.12 (bdl)	41.5 (45)
I-5 11/2/08	Total				33.56	33.56	100 (140)	9.5 (11)	10.19	0.68 (bdl)	53.2 (57.6)	1.16	2.59	1.87	2.17	3.53	31.3 (21)	196 (266)
I-5 11/2/08	Dissolved				35 (36)	35 (36)	100 (140)	9.5 (11)	9.14	0.19 (bdl)	17.8 (30)	<0.05	2.53	1.78	2.38	1.36	0.3 (2)	60 (107)
I-5 11/2/08	Total				21.82	21.82	57 (65)	5.88 (7.2)	6.66	0.41 (bdl)	36.8 (39)	0.738	1.62	1.26	1.66	1.81	13.4 (13.1)	129 (137)
I-5 11/2/08	Dissolved				22.7 (24)	22.7 (24)	57 (65)	5.88 (7.2)	5.96	0.06 (bdl)	12.8 (20.4)	<0.05	1.5	1.14	1.61	0.76	0.14 (3)	46 (109)
I-5 11/20/08	Total				30.32	30.32	118 (89)	6.3 (5.8)	9.52	0.73 (bdl)	60.9 (59.1)	1.68	1.69	1.69	2.06	3.32	28.4 (17.5)	219 (183)
I-5 11/20/08	Dissolved				29 (30)	29 (30)	118 (89)	6.3 (5.8)	7.85	0.25 (bdl)	17.3 (39.6)	<0.05	1.42	1.3	1.8	1.46	0.64 (10.1)	80 (126)
Wemmes 11/20/08	Total				10.95	10.95	26.6	3.69	2.97	0.081	6.05	0.639	0.51	0.76	0.78	0.53	2.01	31.6
Wemmes 11/20/08	Dissolved				10.46	10.46	26.6	3.69	2.6	0.051	3.19	<0.05	0.52	0.62	0.87	0.27	0.224	17.4
Wemmes 12/1/08	Total				16.73	16.73	69 (53)	154 (14)	3.17	0.12 (bdl)	7.9 (9.7)	1.29	0.16	2.14	0.94	0.7	10.4 (2.6)	41 (43)
Wemmes 12/1/08	Dissolved				15.6 (16)	15.6 (16)	69 (53)	154 (14)	2.48	0.03 (bdl)	2.3 (7.9)	<0.05	0.14	1.8	0.75	0.12	bdl (1.8)	12 (28)
Wemmes 1/6/09	Total				154.86	154.86	49.7 (85)	2.56 (2.7)	12.05	0.16 (bdl)	11.1 (2.5)	0.77	0.18	>15 (30.3)	2.84	0.51	7.19 (5.6)	39.0 (46.5)
Wemmes 1/6/09	Dissolved				148.40	148.40	49.7 (85)	2.56 (2.7)	11.61	0.14 (bdl)	5.2 (8.4)	0.2	0.2	>15 (29.0)	3.07	0.26	bdl (3)	23.9 (35.6)
Wemmes 3/11/09	Total				489.69	489.69	108.6	5.97 (2)	>15 (21.3)	bdl (bdl)	21.9 (24)	1.77	0.12	>15 (106)	8.9	7.2	25.5 (17.8)	138 (93.3)
Wemmes 3/11/09	Dissolved				476.6 (440)	476.6 (440)	108.6 (100)	5.97	>15 (21.0)	bdl (bdl)	3.84 (12.7)	0.006	<0.05	>15 (103)	9.62	4.32	13 (4.5)	70.7 (53.1)
Wemmes 3/16/09	Total				93.03	93.03	29.4	2.04 (1.6)	11.2	bdl (bdl)	2.09 (6.8)	0.52	0.36	>15 (15.8)	1.71	3.48	6.92 (4.7)	58.6 (34.3)
Wemmes 3/16/09	Dissolved				88.4	88.4	29.4 (41)	2.04	11.21	bdl (bdl)	1.9 (3.3)	0.009	0.36	>15 (16.5)	1.83	2.81	bdl (bdl)	44.6 (22.7)
Wemmes 3/24/09	Total				14.44	14.44	61.8	2.5 (1.9)	11.29	bdl (bdl)	9.08 (12.1)	0.6	0.26	>15 (27.5)	1.52	3.34	12.4 (7.4)	78.8 (61.4)
Wemmes 3/24/09	Dissolved				136.3 (140)	136.3 (140)	61.8 (57)	2.5	10.9	bdl (bdl)	3.02 (11)	0.003	0.36	>15 (26.5)	1.68	2.18	0.3 (5.6)	48.1 (40.4)
Wemmes 5/5/09	Total				14.63	14.63	116.5 (117)	1.96 (2.3)	2.81	bdl	13.4	0.79	0.46	1.85	0.55	1.3	14	61.5
Wemmes 5/5/09	Dissolved				9.61 (17)	9.61 (17)	116.5 (117)	1.96 (6.3)	1.64	bdl	3.1	0.42	1.34	0.56	1.1	1.6	18.7	18.7

Figure A.10: Data from Herrera sites

Sample	Anions					Storm					AADT # vehicles
	Cl ppm	NO ₂ ppm	NO ₃ ppm	PO ₄ ppm	SO ₄ ppm	ADP hrs	Tot Rainfall in	Duration hrs	Avg Intensity in/hr	Max. Discharge L/s	
Bend 12/29/08						12.5	0.43	11.75	0.0366		24,000
Bend 12/29/08	17.48	bdl	0.768	.076 (0.15)	1.42	12.5	0.43	11.75	0.0366		24,000
Bend 3/16/09						<24	0.09	9	0.0100	18.6	24,000
Bend 3/16/09	55.8078	bdl	1.961	bdl (.078)	2.469	<24	0.09	9	0.0100	18.6	24,000
I-5 3/17/08						14	0.45	11	0.0409	148,500	130,000
I-5 3/17/08	16.70	0.26	4.34	bdl (.0056)	6.86	14	0.45	11	0.0409	148,500	130,000
I-5 10/6/08 #1						12	0.17	11	0.0155	23,810	130,000
I-5 10/6/08 #1	3.66	0.13	5.85 (0.66)	bdl (.026)	6.19	12	0.17	11	0.0155	23,810	130,000
I-5 10/6/08 #2						12	0.17	11	0.0155	23,810	130,000
I-5 10/6/08 #2	3.66	bdl	2.62 (0.66)	0.219 (.026)	6.26	12	0.17	11	0.0155	23,810	130,000
I-5 11/2/08						12	0.29	25	0.0116	23,500	130,000
I-5 11/2/08	3.52	0.29	3.86 (0.68)	bdl (bdl)	6.50	12	0.29	25	0.0116	23,500	130,000
I-5 11/3/08						14	0.92	26	0.0354	22,310	130,000
I-5 11/3/08	2.13	0.19	1.95 (0.41)	bdl (.014)	3.33	14	0.92	26	0.0354	22,310	130,000
I-5 11/20/08						175	0.48	11	0.0436	19,230	130,000
I-5 11/20/08	3.42	0.35	2.47 (0.41)	bdl (.062)	5.29	175	0.48	11	0.0436	19,230	130,000
Wemme 11/20/08											12,000
Wemme 11/20/08	2.42	bdl	0.56	bdl	1.17						12,000
Wemme 12/1/08						30.8	1.02	8.7	0.1172	13,220	12,000
Wemme 12/1/08	6.31	bdl	0.38 (bdl)	bdl (.0085)	0.43	30.8	1.02	8.7	0.1172	13,220	12,000
Wemme 1/6/09						73.7	2.11	37	0.0570	9,910	12,000
Wemme 1/6/09	115.76	bdl	0.529	bdl (<0.005)	3.48	73.7	2.11	37	0.0570	9,910	12,000
Wemme 3/11/09						19.6	0.34	6	0.0567	4.73	12,000
Wemme 3/11/09	488.799	bdl	1.277	bdl (<1)	12.869	19.6	0.34	6	0.0567	4.73	12,000
Wemme 3/16/09						97.3	2.11	48.2	0.0438	10.17	12,000
Wemme 3/16/09	74.3	bdl	0.365	bdl (<0.005)	3.201	97.3	2.11	48.2	0.0438	10.17	12,000
Wemme 3/24/09						10	0.5	24.3	0.0206	3.96	12,000
Wemme 3/24/09	124.8	bdl	0.365	bdl (<0.005)	4.03	10	0.5	24.3	0.0206	3.96	12,000
Wemme 5/5/09						15	1.18	23	0.0513	13.59	12,000
Wemme 5/5/09	2.611	bdl	0.406	bdl	0.52	15	1.18	23	0.0513	13.59	12,000

Figure A.11: Data from Herrera sites, continued

Sample	Sample Type	Tot or Diss	pH	Conductivity µS/cm	Salinity psu	Alkalinity mg/L as CaCO ₃	Hardness mg/L as CaCO ₃	TSS mg/L	DOC mg/L	Cations									
										Ca	Cd	Cu	Fe	K	Mg	Na	Ni	Pb	Zn
Dixon 11/20/08 Composite	Composite	Total	6.6	48.15	0.021	4.45	9.72	27.6	4.77	2.92	0.11	8.82	0.718	0.75	0.59	1.12	0.55	2.82	43.78
Dixon 11/20/08 Composite	Composite	Dissolved					8.37	27.6	4.77	2.56	0.03	4.43	<0.05	0.74	0.48	1.11	0.01	bdl	19.24
Dixon 11/20/08 First Flush	First Flush	Total	6.52	53.15	0.025	7.09	22.31	50.2	13.52	6.66	0.13	14.64	0.824	1.42	1.38	1.9	0.88	5.6	95.18
Dixon 11/20/08 First Flush	First Flush	Dissolved					19.10	50.2	13.52	5.82	0.11	9.02	<0.05	1.44	1.11	1.83	0.46	0.34	45.56
Dixon 12/17/08 Composite	Composite	Total	6.26	21.8	0.008	4.19	5.75	24.8	1.81	1.81	0.02	4.74	<0.05	0.32	0.44	0.81	0.95	2.64	26.08
Dixon 12/17/08 Composite	Composite	Dissolved					5.75	24.8	1.81	1.81	0.02	4.74	<0.05	0.32	0.44	0.81	0.95	2.64	26.08
Dixon 12/17/08 First Flush	First Flush	Total	6.3	113	0.051	13.56	41.04	26.6	14.2	13.44	0.199	24.11	1.3	1.54	2.44	2.46	2.39	5.97	109.79
Dixon 12/17/08 First Flush	First Flush	Dissolved					43.61	26.6	14.2	13.44	0.199	24.11	1.3	1.54	2.44	2.46	2.39	5.97	109.79
Dixon 2/6/09 Composite	Composite	Total	7.31	42.5	0.018	10.02	70.52	34.5	4.24	3.96	1.75	11	0.69	0.5	1.09	0.86	1.32	0.1	49.06
Dixon 2/6/09 Composite	Composite	Dissolved					14.38	34.5	4.24	3.96	1.75	11	0.69	0.5	1.09	0.86	1.32	0.1	49.06
Dixon 2/6/09 First Flush	First Flush	Total	7.38	172.5	0.077	20.58	63.11	155.8	15.57	>15(19.8)	2.24	37.5	2.33	1.2	5.12	3.62	16.9	102.7	301.6
Dixon 2/6/09 First Flush	First Flush	Dissolved					13.48	155.8	15.57	>15(19.8)	1.87	12.2	0.027	1.07	4.29	3.6	12.1	83	79.4
Dixon 2/23/09 Composite	Composite	Total	7.27	23.9	0.009	6.91	8.13	162.2	2.62	2.35	bdl	3.61	0.031	0.37	0.55	0.85	1.44	bdl	34.9
Dixon 2/23/09 Composite	Composite	Dissolved					48.47	162.2	2.62	2.35	bdl	3.61	0.031	0.37	0.55	0.85	1.44	bdl	34.9
Dixon 2/23/09 First Flush	First Flush	Total	7.19	123	0.054	18.55	47.06	18.5	18.45	13.98	bdl	20.9	0.025	0.98	2.95	3.3	5.16	bdl	76.2
Dixon 2/23/09 First Flush	First Flush	Dissolved					47.06	18.5	18.45	13.98	bdl	20.9	0.025	0.98	2.95	3.3	5.16	bdl	76.2
Dixon 3/14/09 Comp	Composite	Total	6.61	16.3	0.006	4.3	6.06	14.5	2.08	1.8	bdl	5.6	0.26	0.3	0.38	1.08	2.1	8.18	43.2
Dixon 3/14/09 Comp	Composite	Dissolved					6.06	14.5	2.08	1.8	bdl	5.6	0.26	0.3	0.38	1.08	2.1	8.18	43.2
Dixon 3/14/09 First Flush	First Flush	Total	6.8	140	0.063	9.75	52.23	122.5	16.02	>15(17.2)	bdl	42.5	1.97	1.23	3.45	5.35	9.4	28.5	303
Dixon 3/14/09 First Flush	First Flush	Dissolved					57.16	122.5	16.02	>15(17.2)	bdl	42.5	1.97	1.23	3.45	5.35	9.4	28.5	303
Dixon 4/12/09 Composite	Composite	Total	6.64	23	0.01	6.66	8.40	23.8	4.79	2.54	bdl	12	0.995	0.83	0.5	2.83	2.1	17.3	69.2
Dixon 4/12/09 Composite	Composite	Dissolved					8.40	23.8	4.79	2.54	bdl	12	0.995	0.83	0.5	2.83	2.1	17.3	69.2
Dixon 4/12/09 First Flush	First Flush	Total	6.68	71.7	0.036	10.21	30.85	125.9	27.44	9.55	bdl	55.3	1.48	1.54	1.7	4.88	7.05	20.9	214
Dixon 4/12/09 First Flush	First Flush	Dissolved					30.85	125.9	27.44	9.55	bdl	55.3	1.48	1.54	1.7	4.88	7.05	20.9	214
Dixon 5/13/09 Composite	Composite	Total	6.58	27.8	0.011	5.91	11.66	27.4	10.78	8.7	bdl	35.6	0.146	1.6	1.34	5.11	4.53	1.7	83.4
Dixon 5/13/09 Composite	Composite	Dissolved					11.66	27.4	10.78	8.7	bdl	35.6	0.146	1.6	1.34	5.11	4.53	1.7	83.4
Dixon 5/13/09 First Flush (#1)	First Flush	Total	6.41	78	0.04	12.4	37.29	87.5	37	11.47	bdl	41	0.8	1.99	2.1	3.72	7.8	11.7	171.3
Dixon 5/13/09 First Flush (#1)	First Flush	Dissolved					37.29	87.5	37	11.47	bdl	41	0.8	1.99	2.1	3.72	7.8	11.7	171.3
Dixon 10/13/09 First Flush	First Flush	Total	7.08	15.6	0.007	11.2	28.13	70.1	15.79	9.23	bdl	11.5	0.0563	1.47	1.27	2.25	bdl	bdl	41.6
Dixon 10/13/09 First Flush	First Flush	Dissolved					28.13	70.1	15.79	9.23	bdl	11.5	0.0563	1.47	1.27	2.25	bdl	bdl	41.6
Dixon 10/13/09 Composite	Composite	Total	7.04	16.4	0.006	8.01	9.42	18.1	4.9	3.08	bdl	3.28	0.0263	0.79	0.42	1.61	bdl	bdl	56.2
Dixon 10/13/09 Composite	Composite	Dissolved					9.42	18.1	4.9	3.08	bdl	3.28	0.0263	0.79	0.42	1.61	bdl	bdl	56.2

Figure A.12: Dixon Outfall composite and first flush data

Sample	Anions						Storm					
	Cl	NO ₂	NO ₃	PO ₄	SO ₄	ADP	Tot Rainfall	Duration	Avg Intensity	Max. Discharge	AADT	
	ppm	ppm	ppm	ppm	ppm	hrs	in	hrs	in/hr	L/s	# vehicles	
Dixon 11/20/08 Composite						172	0.3	9	0.0333	0.415	8,000	
Dixon 11/20/08 Composite	3.27	bdl	1.15	bdl	1.01	172	0.3	9	0.0333	0.415	8,000	
Dixon 11/20/08 First Flush						172	0.3	9	0.0333	0.415	8,000	
Dixon 11/20/08 First Flush	1.74	bdl	6.44	bdl	3.03	172	0.3	9	0.0333	0.415	8,000	
Dixon 12/1/08 Composite						245	0.16	8	0.0200	0.339	8,000	
Dixon 12/1/08 Composite	0.77	bdl	1.33	bdl	0.32	245	0.16	8	0.0200	0.339	8,000	
Dixon 12/1/08 First Flush						245	0.16	8	0.0200	0.339	8,000	
Dixon 12/1/08 First Flush	8.39	bdl	14.73	bdl	6.85	245	0.16	8	0.0200	0.339	8,000	
Dixon 2/6/09 Composite						188	0.27	13.5	0.0200	0.181	8,000	
Dixon 2/6/09 Composite	2.27	bdl	2.509	bdl	1.11	188	0.27	13.5	0.0200	0.181	8,000	
Dixon 2/6/09 First Flush						188	0.27	13.5	0.0200	0.181	8,000	
Dixon 2/6/09 First Flush	29.75	bdl	15.841	bdl	8.24	188	0.27	13.5	0.0200	0.181	8,000	
Dixon 2/23/09 Composite						109	0.7	23	0.0304	0.388	8,000	
Dixon 2/23/09 Composite	1.179	bdl	1.623	bdl	0.532	109	0.7	23	0.0304	0.388	8,000	
Dixon 2/23/09 First Flush						109	0.7	23	0.0304	0.388	8,000	
Dixon 2/23/09 First Flush	9.545	bdl	16.308	bdl	6.823	109	0.7	23	0.0304	0.388	8,000	
Dixon 3/14/09 Comp						109	0.77	24	0.0321	0.316	8,000	
Dixon 3/14/09 Comp	1.107	bdl	0.794	bdl	0.319	109	0.77	24	0.0321	0.316	8,000	
Dixon 3/14/09 First Flush						109	0.77	24	0.0321	0.316	8,000	
Dixon 3/14/09 First Flush	34.008	bdl	6.832	bdl	5.712	109	0.77	24	0.0321	0.316	8,000	
Dixon 4/12/09 Composite						235	0.22	6	0.0367	0.215	8,000	
Dixon 4/12/09 Composite	1.016	bdl	1.167	bdl	0.53	235	0.22	6	0.0367	0.215	8,000	
Dixon 4/12/09 First Flush						235	0.22	6	0.0367	0.215	8,000	
Dixon 4/12/09 First Flush	6.166	bdl	7.358	bdl	4.957	235	0.22	6	0.0367	0.215	8,000	
Dixon 5/13/09 Composite						141	0.17	5.5	0.0309	0.339	8,000	
Dixon 5/13/09 Composite	1.527	bdl	0.584	bdl	0.972	141	0.17	5.5	0.0309	0.339	8,000	
Dixon 5/13/09 First Flush (#1)						141	0.17	5.5	0.0309	0.339	8,000	
Dixon 5/13/09 First Flush (#1)	6.12	bdl	8.01	bdl	7.64	141	0.17	5.5	0.0309	0.339	8,000	
Dixon 10/13/09 First Flush						340	0.39	14.5	0.0269	0.979	8,000	
Dixon 10/13/09 First Flush	1.471	0.245	15.409	bdl	5.345	340	0.39	14.5	0.0269	0.979	8,000	
Dixon 10/13/09 Composite						340	0.39	14.5	0.0269	0.979	8,000	
Dixon 10/13/09 Composite	0.867	bdl	2.299	bdl	1.279	340	0.39	14.5	0.0269	0.979	8,000	

Figure A.13: Dixon Outfall composite and first flush data, continued

Sample	Sample Type	Tot/Diss	pH	Conductivity µS/cm	Salinity psu	Alkalinity mg/L as CaCO ₃	Hardness mg/L as CaCO ₃	TSS mg/L	DOC mg/L	Ca ppm	Cd ppm	Cu ppm	Fe ppm	K ppm	Mg ppm	Na ppm	Ni ppm	Pb ppm	Zn ppm
Dixon 10/2/08 #1	Grab	Total	7.08	44.3	0.0193	10.26	12.13	7.5	5.17	3.932	0.55	9.43	0.225	0.987	0.852	1.285	1.01	13.01	42.22
Dixon 10/2/08 #1	Grab	Dissolved																	
Dixon 10/2/08 #2	Grab	Total	7.08	44.3	0.0193	10.26	12.13	7.5	5.17	3.731	0.05	7.06	<0.05	0.863	0.5	1.286	0.39	bd	22.04
Dixon 10/2/08 #2	Grab	Dissolved																	
Dixon 10/2/08 #2	Grab	Total	7.17	41.03	0.0178	9.75	11.08	6.2	5.26	3.638	0.11	8.94	0.274	1.46	0.57	2.75	0.66	3.23	62.54
Dixon 10/2/08 #2	Grab	Dissolved																	
Dixon 10/2/08	Grab	Total	6.83	104	0.0482	10.55	17.25	7.2	10.44	5.74	0.13	11.55	0.206	0.874	0.93	1.69	0.745	2.83	46.8
Dixon 10/2/08	Grab	Dissolved																	
Dixon 10/2/08	Grab	Total	6.95	56.33	0.024	8.84	16.20	58.7	13.79	5.73	0.14	16.37	0.847	1.38	0.86	1.57	0.98	5.74	72.56
Dixon 10/2/08	Grab	Dissolved																	
Dixon 10/2/08	Grab	Total	6.87	45.2	0.019	7.3	14.81	10.1	20.3	4.85	0.31	16.8	0.471	1.34	1.17	1.09	1.26	3.96	72.95
Dixon 10/2/08	Grab	Dissolved																	
Dixon 10/2/08 #1	Flow	Total	6.83	19.25	0.007	3.18	5.71	14	9.19	1.93	0.21	6.86	0.341	0.53	0.44	0.63	0.57	9.72	31.66
Dixon 10/2/08 #1	Flow	Dissolved																	
Dixon 10/2/08 #2	Flow	Total	7.18	25.65	0.01	6.07	8.52	14.1	3.93	2.56	0.09	5.89	0.377	0.47	0.68	0.75	1.33	2.93	78.15
Dixon 10/2/08 #2	Flow	Dissolved																	
Dixon 10/2/08 #3	Flow	Total	6.99	27.95	0.011	6.12	10.75	21	4.61	3.49	0.08	8.4	0.526	0.47	0.79	0.51	0.73	3.17	88.28
Dixon 10/2/08 #3	Flow	Dissolved																	
Dixon 10/2/08 Bottle 2 (of 5)	Flow	Total	6.21	24.9	0.01	3.18	6.13	38.8	2.59	2.42	0.11	7	0.712	0.71	0.66	1.34	0.39	3.25	47.29
Dixon 10/2/08 Bottle 3 (of 5)	Flow	Dissolved																	
Dixon 10/2/08 Bottle 4 (of 5)	Flow	Total	6.83	113	0.02	18	16.3	163	0.02	0.05	1.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	22.11
Dixon 10/2/08 Bottle 5 (of 5)	Flow	Dissolved																	
Dixon 12/4/08 Bottle 2 (of 6)	Flow	Total	6.83	113	0.02	18	16.3	163	0.02	0.05	1.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	9.27
Dixon 12/4/08 Bottle 3 (of 6)	Flow	Dissolved																	
Dixon 12/4/08 Bottle 4 (of 6)	Flow	Total	6.83	113	0.02	18	16.3	163	0.02	0.05	1.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	14.3
Dixon 12/4/08 Bottle 5 (of 6)	Flow	Dissolved																	
Dixon 12/4/08 Bottle 6 (of 6)	Flow	Total	6.83	113	0.02	18	16.3	163	0.02	0.05	1.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	7.77
Dixon 12/4/08 Bottle 7 (of 6)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #2 (of 10)	Flow	Total	6.51	33.7	0.014	6.4	28.29	67.5	16.75	9.23	bd	17.7	0.901	1.53	1.76	3	1.49	11.8	103.8
Dixon 2/6/09 Bottle #3 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #4 (of 10)	Flow	Total	6.51	4.7	0.001	4.95	11.05	51	16.75	8.92	bd	10.3	0.0444	1.4	1.46	2.68	bd	bd	52.6
Dixon 2/6/09 Bottle #5 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #6 (of 10)	Flow	Total	6.83	4.7	0.001	4.95	11.05	51	16.75	8.92	bd	10.3	0.0444	1.4	1.46	2.68	bd	bd	5.34
Dixon 2/6/09 Bottle #7 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #8 (of 10)	Flow	Total	7.05	8.66	0.001	3.3	8.66	51	9.79	3.51	bd	7.28	0.0496	0.86	0.88	2.5	bd	bd	23.4
Dixon 2/6/09 Bottle #9 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #10 (of 10)	Flow	Total	7.31	7.53	0.001	3.3	8.66	51	9.79	3.51	bd	7.28	0.0496	0.86	0.88	2.5	bd	bd	18.3
Dixon 2/6/09 Bottle #11 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #12 (of 10)	Flow	Total	6.97	6.97	0.001	3.3	8.66	51	9.79	3.51	bd	7.28	0.0496	0.86	0.88	2.5	bd	bd	19.3
Dixon 2/6/09 Bottle #13 (of 10)	Flow	Dissolved																	
Dixon 2/6/09 Bottle #14 (of 10)	Flow	Total	6.89	6.89	0.001	3.3	8.66	51	9.79	3.51	bd	7.28	0.0496	0.86	0.88	2.5	bd	bd	10.3
Dixon 2/6/09 Bottle #15 (of 10)	Flow	Dissolved																	
Dixon 5/19/09 #1	Flow	Total	6.89	60	0.025	9.27	22.07	39	25.08	6.53	bd	34.2	0.393	1.57	1.4	2.72	5.07	5.11	147.4
Dixon 5/19/09 #2	Flow	Dissolved																	
Dixon 5/19/09 #3	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #4	Flow	Dissolved																	
Dixon 5/19/09 #5	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #6	Flow	Dissolved																	
Dixon 5/19/09 #7	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #8	Flow	Dissolved																	
Dixon 5/19/09 #9	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #10	Flow	Dissolved																	
Dixon 5/19/09 #11	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #12	Flow	Dissolved																	
Dixon 5/19/09 #13	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #14	Flow	Dissolved																	
Dixon 5/19/09 #15	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #16	Flow	Dissolved																	
Dixon 5/19/09 #17	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #18	Flow	Dissolved																	
Dixon 5/19/09 #19	Flow	Total	6.89	60	0.025	9.27	20.87	39	25.08	6.43	bd	24.5	0.393	1.56	1.17	3.07	2.67	1.31	79.3
Dixon 5/19/09 #20	Flow	Dissolved																	

Figure A.14: Dixon Outfall grab and flow-weighted sample data

Sample	Anions						Storm						AADT # vehicles
	Cl ppm	NO ₂ ppm	NO ₃ ppm	PO ₄ ppm	SO ₄ ppm	Flow L/s	Wt/ot	ADP hrs	Tot Rainfall in	Duration hrs	Avg Intensity in/hr	Max Discharge L/s	
Dixon 10/2/08 #1								199	0.76	31	0.0245		8,000
Dixon 10/3/08 #1	0.71	bdl	2.50	0.21	1.30			199	0.76	31	0.0245		8,000
Dixon 10/3/08 #2								199	0.76	31	0.0245		8,000
Dixon 10/3/08 #2	0.68	0.16	2.39	bdl	1.10			199	0.76	31	0.0245		8,000
Dixon 10/31/08								227	0.29	10	0.0290		8,000
Dixon 10/31/08	2.59	0.09	5.16	bdl	2.62			227	0.29	10	0.0290		8,000
Dixon 11/2/08								31	0.26	20	0.0130		8,000
Dixon 11/2/08	4.88	bdl	1.57	bdl	1.82			31	0.26	20	0.0130		8,000
Dixon 11/3/08								9	0.68	24	0.0283		8,000
Dixon 11/3/08	1.40	bdl	bdl	0.23	0.84			9	0.68	24	0.0283		8,000
Dixon 11/8/08 #1								36	0.27	6	0.0450		8,000
Dixon 11/8/08 #1	1.46	bdl	0.14	bdl	0.53	0.136	0.254	36	0.27	6	0.0450	0.198	8,000
Dixon 11/8/08 #2								36	0.27	6	0.0450	0.198	8,000
Dixon 11/8/08 #2						0.165	0.563	36	0.27	6	0.0450	0.198	8,000
Dixon 11/8/08 #3	1.15	bdl	0.24	bdl	1.04	0.165	0.563	36	0.27	6	0.0450	0.198	8,000
Dixon 11/8/08 #3						0.136	0.871	38	0.08	1	0.0800	0.150	8,000
Dixon 11/8/08 #3	1.57	bdl	0.63	0.09	0.95	0.136	0.871	38	0.08	1	0.0800	0.150	8,000
Dixon 11/20/08 Bottle 2 (of 5)								172	0.3	9	0.0333	0.415	8,000
Dixon 11/20/08 3-4 (High Flow)								172	0.3	9	0.0333	0.415	8,000
Dixon 11/20/08 3-4 (High Flow)	4.49	bdl	6.27	0.72	0.85			172	0.3	9	0.0333	0.415	8,000
Dixon 11/20/08 Bottle 4 (of 5)								172	0.3	9	0.0333	0.415	8,000
Dixon 11/20/08 Bottle 5 (of 5)								172	0.3	9	0.0333	0.415	8,000
Dixon 12/1/08 Bottle 2 (of 6)						0.15	0.827	245	0.16	8	0.0200	0.339	8,000
Dixon 12/1/08 Bottle 4 (of 6)						0.273	0.684	245	0.16	8	0.0200	0.339	8,000
Dixon 12/1/08 Bottle 6 (of 6)						0.088	0.953	245	0.16	8	0.0200	0.339	8,000
Dixon 2/6/08 Bottle #2 (of 10)						0.165	0.101	188	0.27	13.5	0.0200	0.181	8,000
Dixon 2/6/08 Bottle #4 (of 10)						0.038	0.252	188	0.27	13.5	0.0200	0.181	8,000
Dixon 2/6/08 Bottle #5 (of 10)						0.088	0.331	188	0.27	13.5	0.0200	0.181	8,000
Dixon 2/6/08 Bottle #10 (of 10)						0.011	0.715	188	0.27	13.5	0.0200	0.181	8,000
Dixon 2/23/08 Bottle #3 (of 10)						0.052	0.216	109	0.7	23	0.0304	0.388	8,000
Dixon 2/23/08 Bottle #5 (of 10)						0.215	0.43	109	0.7	23	0.0304	0.388	8,000
Dixon 2/23/08 Bottle #8 (of 10)						0.363	0.75	109	0.7	23	0.0304	0.388	8,000
Dixon 2/23/08 Bottle #10 (of 10)						0.165	0.962	109	0.7	23	0.0304	0.388	8,000
Dixon 3/14/08 Bottle 2 (of 13)						0.15	0.083	109	0.77	24	0.0321	0.316	8,000
Dixon 3/14/08 Bottle 3 (of 13)						0.15	0.165	109	0.77	24	0.0321	0.316	8,000
Dixon 3/14/08 Bottle 5 (of 13)						0.078	0.33	109	0.77	24	0.0321	0.316	8,000
Dixon 3/14/08 Bottle 13 (of 13)						0.027	0.988	109	0.77	24	0.0321	0.316	8,000
Dixon 4/12/08 Bottle 2 (of 3)						0.198	0.391	235	0.22	6	0.0367	0.215	8,000
Dixon 4/12/08 Bottle 3 (of 3)						0.123	0.773	235	0.22	6	0.0367	0.215	8,000
Dixon 5/13/08 Pseudo-First Flush (#4)						0.014	0.025	141	0.17	5.5	0.0309	0.339	8,000
Dixon 5/13/08 Pseudo-First Flush (#4)	5.516	bdl	6.067	bdl	5.707	0.014	0.025	141	0.17	5.5	0.0309	0.339	8,000
Dixon 5/13/08 #5								141	0.17	5.5	0.0309	0.339	8,000
Dixon 5/13/08 #9						0.088	0.127	141	0.17	5.5	0.0309	0.339	8,000
Dixon 5/13/08 #13						0.027	0.535	141	0.17	5.5	0.0309	0.339	8,000
Dixon 5/13/08 #1						0.052	0.945	141	0.17	5.5	0.0309	0.339	8,000
Dixon 9/23/08 #1	5.362	bdl	15.725	bdl	5.883								8,000
Dixon 9/23/08 #2													8,000
Dixon 9/23/08 #2	5.524	bdl	3.676	bdl	2.902								8,000
Dixon 10/13/08 #4	0.44	bdl	2.046	bdl	1.307	0.123	0.15	340	0.39	14.5	0.0269	0.979	8,000
Dixon 10/13/08 #5	0.813	0.205	4.379	bdl	2.07	0.932	0.2	340	0.39	14.5	0.0269	0.979	8,000
Dixon 10/13/08 #11	0.478	bdl	1.88	bdl	0.639	0.66	0.51	340	0.39	14.5	0.0269	0.979	8,000
Dixon 10/13/08 #17	0.489	bdl	1.978	bdl	0.624	0.078	0.81	340	0.39	14.5	0.0269	0.979	8,000
Dixon 10/13/08 #20	3.906	bdl	1.562	bdl	1.094	0.15	0.96	340	0.39	14.5	0.0269	0.979	8,000

Figure A.15: Dixon Outfall grab and flow-weighted sample data, continued

A.4 MINTEQ SPECIATION DATA

The concentration and distribution of 4 copper species, $\text{Cu}^{2+}_{\text{free}}$ (referred to as “CuFree”), Cu-DOM, CuOH^+ , and CuCO_3^{2-} determined from the visual MINTEQ modeling using a Gaussian unimodal DOM model to account for species binding to organics are presented in Figure A.16. Again, these species accounted for over 99% of all copper species in all but one sample, as shown by the column marked “Percent Check”. Concentration data presented in the table is in terms of nM.

Sample	CuFree	LogCuFree	PerCuFree	Cu-DOM	LogCu-DOM	PerCu-DOM	CuOH	LogCuOH	PerCuOH	CuCO3	LogCuCO3	PerCuCO3	Percent Check
Bend 12/29/08	6.91	0.839478647	8.43%	71.28	1.852967691	86.94%	1.44	0.138362492	1.76%	2.24	0.35024802	2.73%	99.86%
Bend 3/16/09	17.49	1.242789809	12.42%	117.45	2.069855021	83.39%	2.16	0.35445751	1.53%	3.44	0.53655844	2.44%	99.79%
Dixon 10/3/08 #1	8.94	0.951337519	8.05%	93.28	1.969788537	83.96%	3.19	0.503790683	2.87%	5.89	0.73158877	4.85%	99.73%
Dixon 10/3/08 #2	8.34	0.921166051	7.67%	90.64	1.957319897	83.35%	3.67	0.564666064	3.38%	5.88	0.76937733	5.41%	99.81%
Dixon 10/31/08	8.9	0.948390007	6.33%	126.92	2.103530063	90.22%	1.74	0.240549248	1.24%	2.97	0.472756645	2.11%	99.89%
Dixon 11/2/08	7.22	0.858537198	4.64%	146.63	2.166227835	94.31%	0.74	-0.130780992	0.48%	0.8	-0.096691	0.51%	99.94%
Dixon 11/3/08	3.58	0.553883027	2.58%	133.95	2.126942718	96.62%	0.49	-0.30980392	0.35%	0.58	-0.236572	0.42%	99.97%
Dixon 11/8/08 #1	2.05	0.311733861	3.06%	64.34	1.808481057	95.98%	0.41	-0.387216143	0.16%	0.22	-0.6575773	0.33%	99.85%
Dixon 11/8/08 #2	5.18	0.71432976	9.17%	48.85	1.688864568	86.47%	2.33	0.367355921	4.12%	0.05	-1.30103	0.09%	99.85%
Dixon 11/19/08 #5	7.61	0.881384657	9.67%	68.51	1.835733968	87.07%	2.2	0.342425681	2.80%	0.28	-0.552842	0.36%	99.89%
Dixon 11/20/08 Composite													
Dixon 11/20/08 First Flush	7.81	0.760422483	8.26%	63.16	1.80042121	90.60%	0.68	-0.167491087	0.98%	0.1	-1	0.14%	99.98%
Dixon 11/20/08 3+4 (High Flow)	5.11	0.7084209	12.73%	133.31	2.124862728	93.92%	0.75	-0.124938737	0.93%	0.03	-1.5228787	0.02%	99.97%
Dixon 12/1/08 Composite	4.65	0.667452953	16.60%	22.91	1.360025089	81.79%	0.25	-0.602059991	0.62%	0.01	-2	0.02%	99.88%
Dixon 2/6/09 Composite	24.01	1.38039216	9.29%	230.25	2.362199639	89.05%	1.34	0.127104798	0.52%	2.39	0.3783979	0.92%	99.89%
Dixon 2/16/09 First Flush	6.91	0.839478647	9.15%	57.95	1.76305344	76.72%	4.19	0.992126076	5.10%	31.41	1.49706794	16.36%	99.49%
Dixon 2/23/09 Composite	6.51	0.813580989	10.86%	45.89	1.661718058	76.54%	3.64	0.561101384	6.07%	3.74	0.5728716	6.24%	99.71%
Dixon 3/14/09 Comp	4.75	0.67669361	12.07%	276.89	2.442307271	84.19%	8.7	0.999519253	2.65%	22.38	1.34986008	6.80%	99.75%
Dixon 3/14/09 First Flush	23.39	1.36903022	8.49%	242.8	2.385248682	88.17%	4.08	0.610660163	1.48%	4.66	0.66838592	1.69%	99.83%
Dixon 4/12/09 Composite	8.57	0.932980822	6.91%	113.42	2.054689643	91.46%	1.12	0.49218023	0.90%	0.83	-0.0809219	0.67%	99.95%
Dixon 4/12/09 First Flush	16.27	1.211387553	2.90%	538.93	2.73153236	96.20%	2.24	0.350248018	0.40%	2.54	0.40483372	0.45%	99.96%
Dixon 5/13/09 Composite	8.46	0.927370363	4.07%	197.31	2.295149097	94.99%	0.97	-0.013228266	0.47%	0.92	-0.0362122	0.44%	99.97%
Dixon 5/13/09 First Flush #1	11.89	1.075181855	2.48%	465.18	2.667621034	96.92%	0.87	-0.060480747	0.18%	1.71	0.23299611	0.36%	99.93%
Dixon 5/13/09 Pseudo-First Flush #1	9.24	0.965671971	2.40%	373.5	2.572290606	96.88%	1.04	0.017033339	0.27%	1.58	0.19885709	0.41%	99.95%
Dixon 9/29/09 #1	8.33	0.920645001	5.14%	152.07	2.182043546	93.82%	0.77	-0.113509275	0.48%	0.78	-0.1079054	0.48%	99.92%
Dixon 9/29/09 #2	5.03	0.701567985	4.39%	108.39	2.04989216	94.61%	0.63	-0.200659451	0.35%	0.45	-0.3467875	0.39%	99.95%
Dixon 10/13/09 First Flush	9.52	0.978636948	5.26%	162.04	2.209622235	89.54%	3.29	0.517195898	1.82%	5.84	0.76641285	3.23%	99.84%
Dixon 10/13/09 Composite	3.94	0.595496222	7.63%	44.63	1.649626887	86.47%	1.29	0.110589971	2.50%	1.69	0.2278867	3.27%	99.87%
Dixon 10/13/09 #1	4.67	0.669316881	6.48%	63.13	1.800235789	87.59%	1.57	0.195899652	2.18%	2.61	0.41664051	3.62%	99.87%
Dixon 10/13/09 #5	4.88	0.688419822	5.96%	67.32	1.828144107	82.27%	2.93	0.46686762	3.58%	6.49	0.8122447	7.93%	99.74%
Dixon 10/13/09 #11	2.71	0.432969291	7.27%	32.2	1.507855872	86.34%	1.03	0.012837225	2.76%	1.31	0.1172713	3.51%	99.88%
Dixon 10/13/09 #17	1.36	0.135538908	8.91%	13.09	1.116939647	85.75%	0.38	-0.402016403	2.49%	0.42	-0.3767507	2.75%	99.90%
Dixon 10/13/09 #20	1.86	0.269512944	8.69%	18.66	1.270911639	87.19%	0.43	-0.366531544	2.01%	0.42	-0.3767507	1.96%	99.85%
1-5 3/17/08	20.07	1.302547372	9.66%	159.99	2.204092838	77.02%	4.64	0.666517981	2.23%	22.05	1.34340859	10.62%	99.53%
1-5 10/16/08 #1	40.07	1.602819342	11.20%	271.39	2.433593841	75.87%	11.17	1.048051173	3.12%	33.13	1.52022144	9.26%	99.46%
1-5 11/2/08	22.81	1.358125285	8.14%	219.47	2.341375164	78.35%	9.2	0.963787827	3.28%	27.64	1.44153804	9.87%	99.65%
1-5 11/3/08	20.32	1.307923704	10.09%	165.05	2.217615529	81.94%	4.81	0.682145076	2.39%	10.73	1.03059972	5.33%	99.74%
1-5 11/20/08	31.11	1.492900011	11.43%	234.95	2.370975449	86.30%	1.56	0.193124598	0.57%	3.79	0.57863921	1.39%	99.69%
Wemme 11/20/08	4.86	0.686636269	9.68%	44.59	1.649237472	88.83%	0.41	-0.387216143	0.82%	0.3	-0.5228787	0.60%	99.92%
Wemme 12/1/08	7.7	0.886490725	21.27%	27.48	1.439016728	75.92%	0.59	-0.229147988	1.65%	0.37	-0.4317983	1.02%	99.85%
Wemme 1/6/09	25.84	1.412925209	31.58%	37.94	1.579097327	46.36%	7.22	0.858537198	8.82%	10.22	1.0094509	12.49%	98.25%
Wemme 3/11/09	19.59	1.292034436	32.42%	31.27	1.495127881	51.75%	2.94	0.46834733	4.87%	5.89	0.77011529	9.50%	99.33%
Wemme 3/16/09	10.46	1.019531685	34.98%	14.3	1.153336037	47.83%	2.1	0.322219295	7.02%	2.84	0.45331834	9.50%	99.30%
Wemme 3/24/09	16.2	1.209515015	34.09%	24.48	1.388811413	51.51%	2.61	0.416640507	5.49%	3.9	0.59106461	8.21%	99.95%
Wemme 5/5/09	6.72	0.827369273	13.78%	40.81	1.610766595	83.66%	0.77	-0.113509275	1.58%	0.46	-0.3372422	0.94%	99.95%

Figure A.16: Visual MINTEQ raw copper speciation data

The following tables are complete summary of the cation-complex concentrations and copper complexation determined in each of the three DOM models used to model the composite samples that were compared with analytical speciation results.

Table A.5: Summary of cation-DOM complexes determined for each model and sample (1 of 2)

Sample	Model	Calcium	Magnesium	Hydrogen	Zinc	Copper	Other
		μM	μM	μM	μM	μM	μM
Bend 12/29/08	Gaussian	3.469	1.070	0.288	0.077	0.067	0.002
	NICA-Donnan	0.409	1.625	15.560	0.003	0.082	0.007
	SHM	0.988	2.384	12.110	0.122	0.082	13.448
Bend 3/16/09	Gaussian	4.087	2.406	0.217	0.131	0.107	0.010
	NICA-Donnan	0.216	1.441	15.814	0.002	0.140	2.930
	SHM	1.144	5.347	13.321	0.185	0.141	12.345
I-5 10/06/08	Gaussian	8.700	0.274	0.207	0.088	0.265	0.002
	NICA-Donnan	1.541	0.967	20.913	0.005	0.356	0.010
	SHM	4.166	1.041	16.151	0.161	0.357	17.536
I-5 11/02/08	Gaussian	11.669	0.383	0.290	0.160	0.225	0.004
	NICA-Donnan	2.072	1.331	28.608	0.009	0.280	0.014
	SHM	5.541	1.429	22.050	0.310	0.280	23.948
I-5 11/03/08	Gaussian	6.199	0.198	0.232	0.107	0.156	0.002
	NICA-Donnan	1.064	0.687	17.910	0.006	0.201	0.007
	SHM	2.596	0.655	13.716	0.191	0.201	15.856
I-5 11/20/08	Gaussian	8.018	0.222	0.229	0.175	0.203	0.005
	NICA-Donnan	1.435	0.818	20.839	0.009	0.271	0.015
	SHM	3.658	0.801	15.960	0.308	0.272	17.891
Dixon 2/06/09	Gaussian	3.462	0.136	0.219	0.064	0.058	0.349
	NICA-Donnan	0.454	0.357	12.264	0.003	0.075	1.077
	SHM	1.202	0.375	9.728	0.078	0.075	12.441
Dixon 2/23/09	Gaussian	1.895	0.073	0.177	0.062	0.044	0.002
	NICA-Donnan	0.208	0.166	7.797	0.002	0.060	0.553
	SHM	0.565	0.174	6.192	0.095	0.060	7.773
Dixon 3/14/09	Gaussian	1.281	0.038	0.174	0.035	0.029	0.006
	NICA-Donnan	0.126	0.083	6.188	0.001	0.039	0.517
	SHM	0.333	0.078	4.948	0.052	0.039	6.366
Dixon 11/20/08	Gaussian	3.855	0.108	0.290	0.052	0.058	0.021
	NICA-Donnan	0.607	0.365	14.896	0.003	0.070	0.037
	SHM	1.268	0.278	11.331	0.093	0.070	14.051
Dixon 4/12/09	Gaussian	3.419	0.102	0.332	0.100	0.104	0.002
	NICA-Donnan	0.376	0.241	14.239	0.003	0.124	1.055
	SHM	1.028	0.238	11.331	0.145	0.124	14.311

Table A.6: Summary of cation-DOM concentrations calculated in each model and sample (2 of 2)

Sample	Model	Calcium	Magnesium	Hydrogen	Zinc	Copper	Other
		μM	μM	μM	μM	μM	μM
Dixon 5/13/09	Gaussian	6.155	0.183	0.520	0.193	0.185	4.112
	NICA-Donnan	1.194	0.731	29.047	0.011	0.208	4.414
	SHM	2.164	0.487	22.563	0.164	0.207	34.241
Dixon 10/13/09	Gaussian	4.010	0.092	0.293	0.112	0.042	0.000
	NICA-Donnan	0.564	0.290	14.998	0.005	0.052	0.471
	SHM	1.344	0.241	11.600	0.198	0.052	14.362
Dixon 12/01/08	Gaussian	1.281	0.034	0.133	0.014	0.019	0.000
	NICA-Donnan	0.190	0.114	5.699	0.001	0.028	0.000
	SHM	0.370	0.078	4.319	0.028	0.028	5.467
Wemme 12/01/08	Gaussian	1.115	0.132	0.098	0.012	0.022	0.000
	NICA-Donnan	0.149	0.286	4.735	0.001	0.036	0.001
	SHM	0.327	0.312	3.644	0.022	0.036	4.385
Wemme 3/11/09	Gaussian	6.268	4.974	0.075	0.049	0.030	0.007
	NICA-Donnan	0.510	4.238	16.433	0.002	0.060	0.123
	SHM	1.778	11.475	13.440	0.109	0.060	6.386
Wemme 11/20/08	Gaussian	2.812	0.112	0.241	0.040	0.040	0.001
	NICA-Donnan	0.426	0.341	11.540	0.002	0.050	0.004
	SHM	0.880	0.276	8.778	0.075	0.050	10.890
Wemme 1/06/09	Gaussian	2.799	1.132	0.054	0.013	0.037	0.000
	NICA-Donnan	0.281	1.370	7.244	0.001	0.081	0.001
	SHM	0.932	3.076	5.825	0.026	0.082	4.335
Wemme 3/16/09	Gaussian	3.731	0.916	0.025	0.034	0.014	0.002
	NICA-Donnan	0.168	0.579	5.639	0.001	0.030	0.163
	SHM	1.663	3.454	4.611	0.073	0.030	0.021
Wemme 3/24/09	Gaussian	2.197	0.864	0.045	0.023	0.019	0.001
	NICA-Donnan	0.204	0.975	5.748	0.001	0.047	0.163
	SHM	0.732	2.351	4.648	0.044	0.047	3.556
Wemme 5/05/09	Gaussian	1.155	0.156	0.154	0.029	0.035	0.001
	NICA-Donnan	0.147	0.318	6.076	0.001	0.049	0.004
	SHM	0.294	0.316	4.643	0.042	0.049	5.772

Table A.7: Summary of free ionic copper concentrations and copper complexation calculated for each model and sample

Date	Site	Gaussian Cufree	Gaussian Cu-DOM Complex	NICA-Donnan Cufree	NICA-Donnan Cu-DOM Complex	SHM Cufree	SHM Cu-DOM Complex
		M	%	M	%	M	%
12/29/2008	Bend	-7.93	81.41	-10.10	99.87	-10.41	99.94
3/16/2009	Bend	-7.59	76.13	-9.16	99.52	-9.77	99.87
10/6/2008	15	-7.18	74.29	-8.96	99.57	-9.40	99.84
11/2/2008	15	-7.40	80.34	-9.50	99.84	-9.84	99.93
11/3/2008	15	-7.47	77.29	-9.41	99.74	-9.77	99.89
11/20/2008	15	-7.34	74.73	-9.24	99.68	-9.57	99.85
11/20/2008	Dixon	-7.99	83.01	-10.31	99.92	-10.58	99.96
12/1/2008	Dixon	-8.14	67.62	-10.29	99.77	-10.64	99.90
2/6/2009	Dixon	-7.87	77.37	-9.96	99.41	-9.83	99.76
2/23/2009	Dixon	-7.90	74.02	-9.74	99.62	-10.17	99.86
3/14/2009	Dixon	-8.07	74.06	-9.93	99.64	-10.39	99.88
4/12/2009	Dixon	-7.80	84.23	-9.62	99.76	-10.11	99.92
5/13/2009	Dixon	-7.74	89.12	-9.96	99.93	-9.13	99.55
10/13/2009	Dixon	-8.13	82.12	-10.57	99.93	-10.70	99.95
11/20/2008	Wemme	-8.08	79.31	-10.38	99.90	-10.67	99.95
12/1/2008	Wemme	-7.94	60.96	-9.81	99.46	-10.24	99.80
1/6/2009	Wemme	-7.45	44.62	-9.15	98.89	-9.60	99.61
3/11/2009	Wemme	-7.64	48.85	-10.20	99.86	-10.22	99.87
3/24/2009	Wemme	-7.66	39.83	-9.45	99.03	-9.83	99.59
5/5/2009	Wemme	-7.94	71.47	-9.78	99.59	-10.18	99.83

A.5 S-PLUS MATRIX PLOTS

This appendix shows matrix plots obtained from S-Plus when modeling $\text{Cu}^{2+}_{\text{diss}}$ and $\text{Cu}^{2+}_{\text{free}}$. The matrix plots are a useful tool because they provide simple visual correlations between an array of variables. The variable above/below a specific plot is represented on the x-axis, while the variable to the left/right of a specific plot is represented on the y-axis.

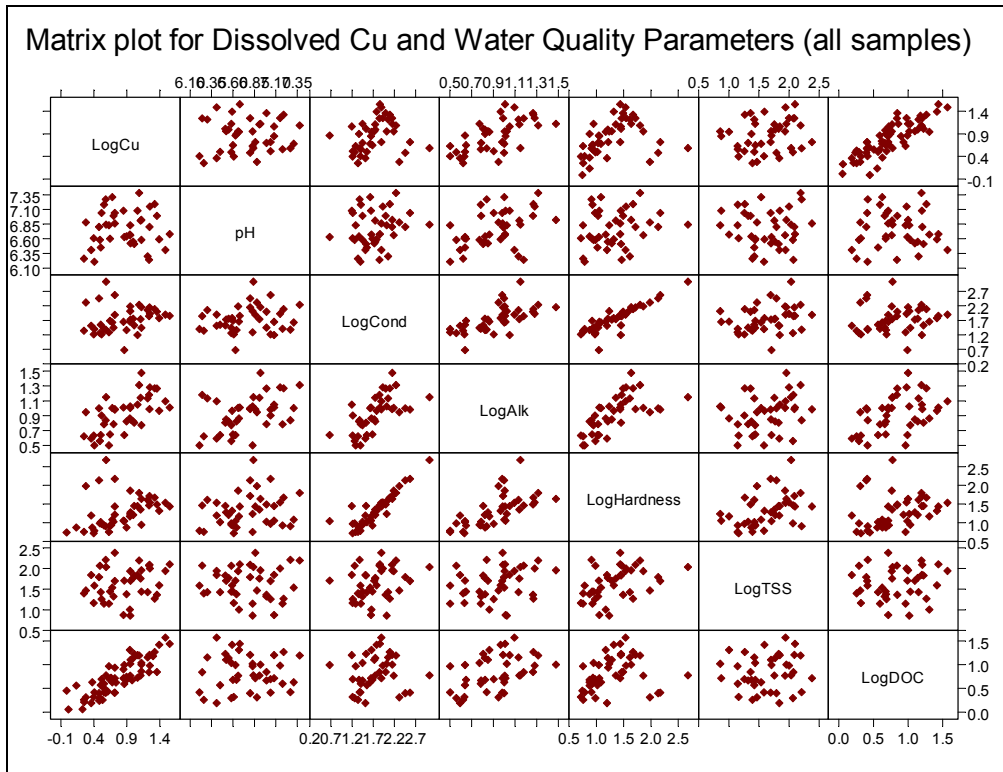


Figure A.17: Dissolved copper – water quality parameters matrix plot

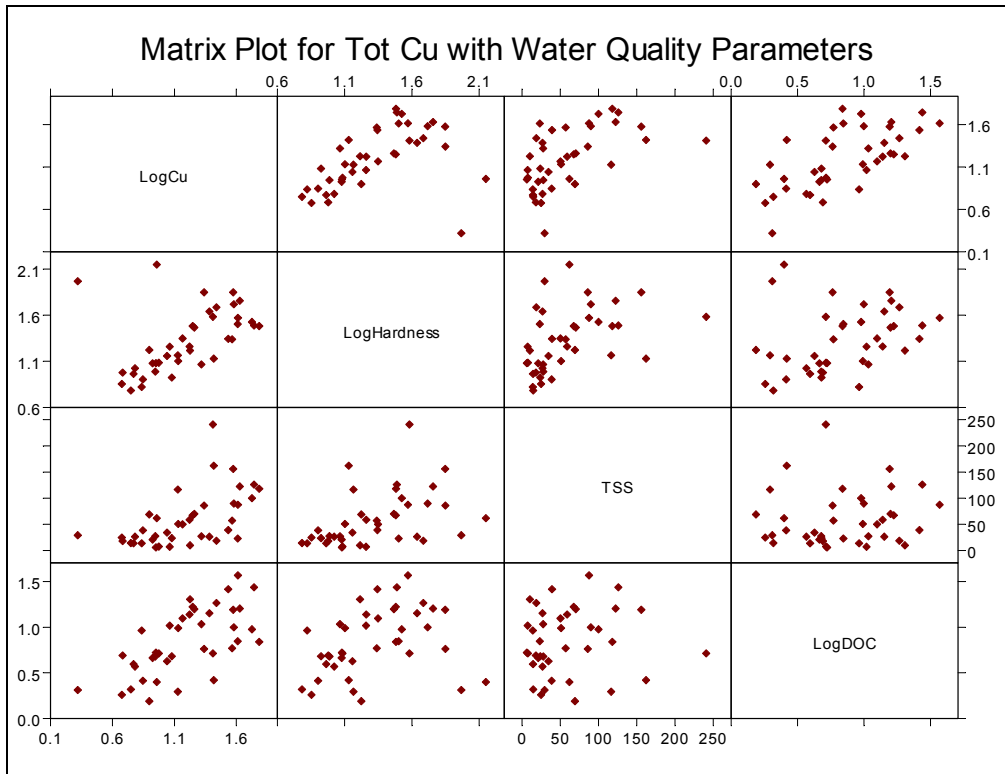


Figure A.18: Total Copper – water quality parameters matrix plot

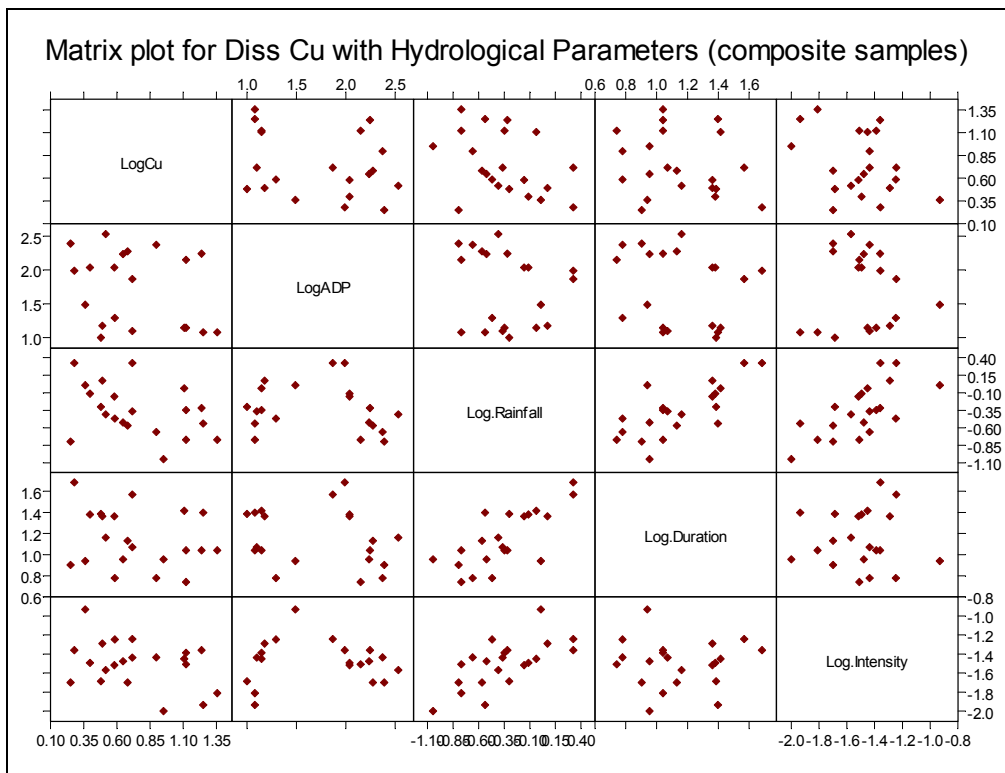


Figure A.19: Dissolved copper – hydrologic variables matrix plot

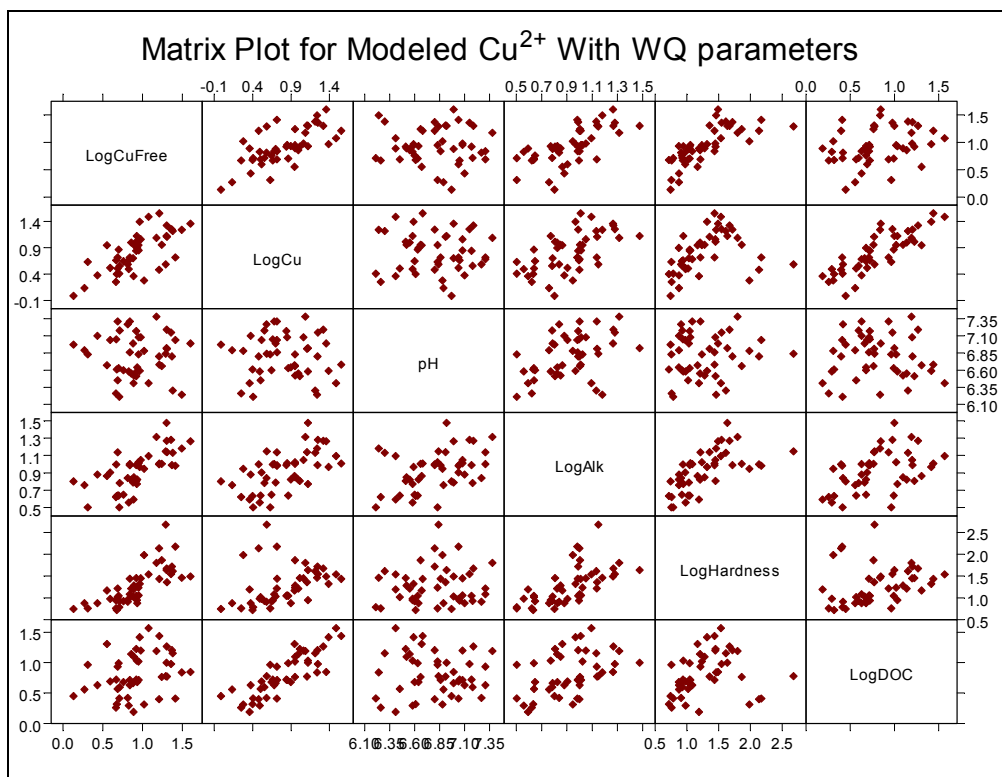


Figure A.20: Modeled Free ionic copper – water quality parameters matrix plot

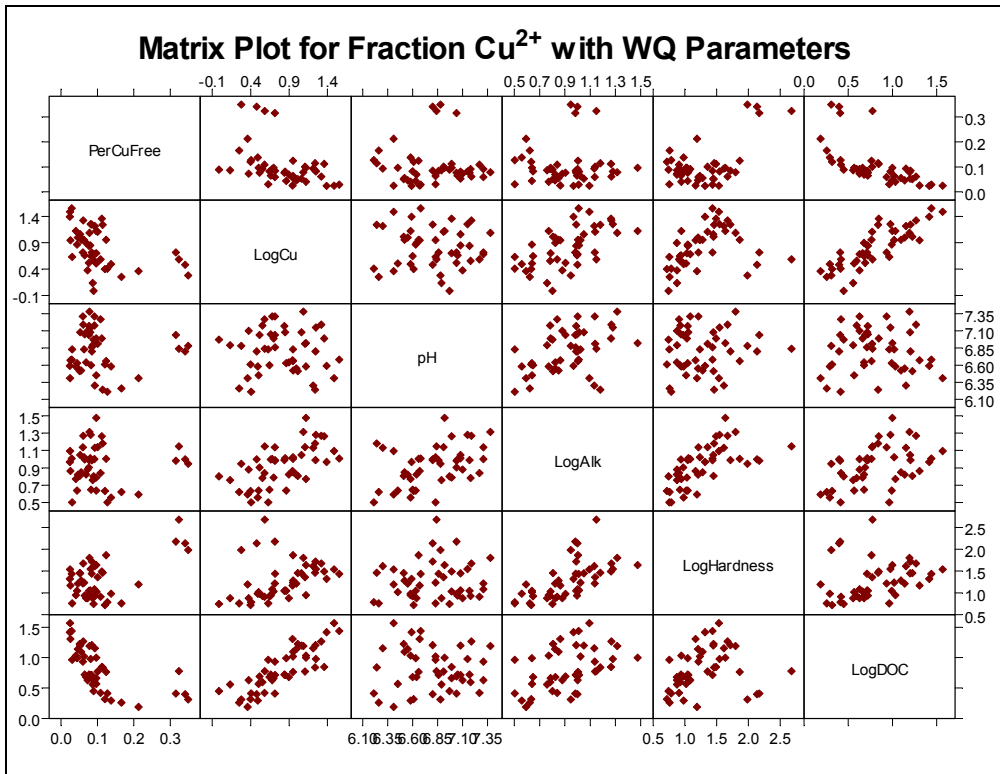


Figure A.21: Modeled Percent Free ionic copper – water quality parameters matrix plotx contains the relevant S-Plus output from the statistics analysis. Annotations denoting the nature of the analysis and any conclusions drawn accompany the output.

Below is the Fisher's LSD simultaneous comparison of LogCu in composite samples at all sites:

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogCu ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	1.674504	0.718946
Deg. of Freedom	3	18

Residual standard error: 0.1998536
 Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	1.674504	0.5581680	13.97465	0.00005991871
Residuals	18	0.718946	0.0399414		

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1009
 response variable: LogCu

intervals excluding 0 are flagged by '*****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.198	0.158	-0.13400	0.5300	
Bend-I-5	-0.380	0.167	-0.73200	-0.0289	*****
Bend-Wemme	0.346	0.160	0.00968	0.6830	*****
Dixon-I-5	-0.578	0.114	-0.81800	-0.3390	*****
Dixon-Wemme	0.148	0.103	-0.06910	0.3660	
I-5-Wemme	0.727	0.117	0.48100	0.9720	*****

The results show the following significant differences in LogCu Levels:

I-5 > Bend: 2.40 times more Cu (1.07-5.40, 95% CI)

Bend > Wemme: 2.22 times more Cu (1.02-4.82, 95% CI)

I-5 > Dixon: 3.78 times more Cu (2.18-6.58, 95% CI)

I-5 > Wemme: 5.33 times more Cu (3.03-9.38, 95% CI)

Below is the Fisher's LSD simultaneous comparison of LogDOC in composite samples at all sites:

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogDOC ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	0.6699371	0.7085800
Deg. of Freedom	3	18

Residual standard error: 0.1984075
 Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	0.6699371	0.2233124	5.672786	0.006465129
Residuals	18	0.7085800	0.0393656		

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1009

response variable: LogDOC

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.150	0.157	-0.1790	0.4800	
Bend-I-5	-0.148	0.166	-0.4970	0.2010	
Bend-Wemme	0.318	0.159	-0.0160	0.6520	
Dixon-I-5	-0.298	0.113	-0.5360	-0.0604	****
Dixon-Wemme	0.168	0.103	-0.0476	0.3840	
I-5-Wemme	0.466	0.116	0.2220	0.7100	****

The results show the following significant differences in LogCu Levels:

I-5 > Dixon: 1.99 times more DOC (1.15-3.44, 95% CI)

I-5 > Wemme: 2.92 times more DOC (1.67-5.13, 95% CI)

Below is the Fisher's LSD simultaneous comparison of LogTotCu in composite samples at all sites:

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogCu ~ Site, data = STATS091028...CompTot, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	1.932551	1.211631
Deg. of Freedom	3	18

Residual standard error: 0.2594472
 Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	1.932551	0.6441835	9.569995	0.0005335319
Residuals	18	1.211631	0.0673128		

Estimated Coefficients:

```
(Intercept) SiteDixon SiteI-5 SiteWemme
1.374617 -0.386052 0.278731 -0.4503735
```

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1009
 response variable: LogCu

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.3860	0.205	-0.0449	0.817	
Bend-I-5	-0.2790	0.217	-0.7350	0.177	
Bend-Wemme	0.4500	0.208	0.0133	0.887	****
Dixon-I-5	-0.6650	0.148	-0.9760	-0.354	****
Dixon-Wemme	0.0643	0.134	-0.2180	0.346	
I-5-Wemme	0.7290	0.152	0.4100	1.050	****

The results show the following significant differences in LogTotCu Levels

I-5 > Dixon: 4.62 times more TotCu (2.26-9.46, 95% CI)

I-5 > Wemme: 5.36 times more TotCu (2.57-11.22, 95% CI)

Bend > Wemme: 2.82 times more TotCu (1.03-7.71, 95% CI)

Below is the regression analysis that examines the effect of AADT. This examines all of the composite samples, including I-5 samples. The 2nd model shows Cu correlated to I5 site association and AADT.

*** Linear Model ***

Call: lm(formula = LogCu ~ AADT, data = STATS091028...CompDiss, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.3284	-0.1105	-0.006719	0.09367	0.5417

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.5369	0.0569	9.4421	0.0000
AADT	0.0000	0.0000	5.8032	0.0000

Residual standard error: 0.2112 on 20 degrees of freedom

Multiple R-Squared: 0.6274

F-statistic: 33.68 on 1 and 20 degrees of freedom, the p-value is 0.00001118

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
AADT	1	1.501657	1.501657	33.67727	0.00001118255
Residuals	20	0.891793	0.044590		

*** Linear Model ***

Call: lm(formula = LogCu ~ I5.ind + AADT, data = STATS091028...CompDiss, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.3248	-0.111	-0.0178	0.1058	0.5602

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.4740	0.1328	3.5689	0.0020
I5.ind	-0.6635	1.2598	-0.5267	0.6045
AADT	0.0000	0.0000	1.0195	0.3208

Residual standard error: 0.2151 on 19 degrees of freedom

Multiple R-Squared: 0.6328

F-statistic: 16.37 on 2 and 19 degrees of freedom, the p-value is 0.00007362

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
I5.ind	1	1.466401	1.466401	31.69836	0.0000199
AADT	1	0.048087	0.048087	1.03947	0.3207511
Residuals	19	0.878961	0.046261		

Based on both of the outputs above, AADT does have a significant direct relationship w/ Cu in composite samples; but only one of the variables – AADT or the I-5 indicator – accounts for this variability

Below is the regression analysis that examines the effect of AADT in non-urban samples. This examines all of the composite samples NOT from I-5.

*** Linear Model ***

Call: lm(formula = LogCu ~ AADT, data = STATS091028...CompDiss.NOI5, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.3248	-0.1236	-0.01925	0.1124	0.5602

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.4740	0.1458	3.2503	0.0054
AADT	0.0000	0.0000	0.9285	0.3678

Residual standard error: 0.2362 on 15 degrees of freedom

Multiple R-Squared: 0.05436

F-statistic: 0.8622 on 1 and 15 degrees of freedom, the p-value is 0.3678

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
AADT	1	0.0480873	0.04808725	0.8621999	0.3678257
Residuals	15	0.8365911	0.05577274		

Based on the above output, there is no significant correlation b/w Cu levels at non-urban sites w/ varying AADTs. This doesn't necessarily mean there isn't a relationship, but we certainly don't have a large enough dataset to find one.

Below is the regression analysis that examines the difference b/w Cu and DOC in FF samples versus composite samples at the Dixon site.

*** Linear Model ***

Call: lm(formula = LogCu ~ FF.ind, data = STATS091028...DixCompFFDiss, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.3858	-0.1597	-0.01027	0.1216	0.4843

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.6362	0.0860	7.3987	0.0000
FF.ind	0.6034	0.1216	4.9614	0.0002

Residual standard error: 0.2432 on 14 degrees of freedom

Multiple R-Squared: 0.6374

F-statistic: 24.62 on 1 and 14 degrees of freedom, the p-value is 0.000209

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
FF.ind	1	1.456205	1.456205	24.61531	0.0002089761
Residuals	14	0.828219	0.059158		

*** Linear Model ***

Call: lm(formula = LogDOC ~ FF.ind, data = STATS091028...DixCompFFDiss, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.3302	-0.1261	-0.0294	0.09492	0.4447

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.5879	0.0740	7.9447	0.0000
FF.ind	0.6768	0.1046	6.4678	0.0000

Residual standard error: 0.2093 on 14 degrees of freedom

Multiple R-Squared: 0.7493

F-statistic: 41.83 on 1 and 14 degrees of freedom, the p-value is 0.00001478

Analysis of Variance Table

Response: LogDOC

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
FF.ind	1	1.832457	1.832457	41.83288	0.0000147835
Residuals	14	0.613259	0.043804		

So both higher Cu and higher DOC concentrations are significantly associated w/ a first-flush phenomenon.

Below is the model-building results for predicting Cu concentrations in composite samples as a function of LogADP (Antecedent Dry period), Log.Rainfall (Total Rainfall), Log.Intensity (Average Rainfall Intensity), AFTER accounting for site associations. Log.Duration (rainfall duration) was screened out as a variable due to covarying with Log.Rainfall.

```

*** Stepwise Regression ***

*** Stepwise Model Comparisons ***
Start: AIC= 1.2383
LogCu ~ I5.ind + Bend.ind + Wemme.ind + LogADP + Log.Rainfall + Log.Intensity

Single term deletions

Model:
LogCu ~ I5.ind + Bend.ind + Wemme.ind + LogADP + Log.Rainfall + Log.Intensity

scale: 0.0458637

      Df Sum of Sq      RSS      Cp
<none>      0.5962280 1.238320
LogADP  1 0.00000841 0.5962365 1.146601
Log.Rainfall  1 0.09246753 0.6886956 1.239060
Log.Intensity  1 0.01391247 0.6101405 1.160505

Step: AIC= 1.1466
LogCu ~ I5.ind + Bend.ind + Wemme.ind + Log.Rainfall + Log.Intensity

Single term deletions

Model:
LogCu ~ I5.ind + Bend.ind + Wemme.ind + Log.Rainfall + Log.Intensity

scale: 0.0458637

      Df Sum of Sq      RSS      Cp
<none>      0.5962365 1.146601
Log.Rainfall  1 0.09480012 0.6910366 1.149674
Log.Intensity  1 0.01538608 0.6116225 1.070259

Step: AIC= 1.0703
LogCu ~ I5.ind + Bend.ind + Wemme.ind + Log.Rainfall

Single term deletions

Model:
LogCu ~ I5.ind + Bend.ind + Wemme.ind + Log.Rainfall

scale: 0.0458637

      Df Sum of Sq      RSS      Cp
<none>      0.6116225 1.070259
Log.Rainfall  1 0.07942346 0.6910460 1.057956

Step: AIC= 1.058
LogCu ~ I5.ind + Bend.ind + Wemme.ind

*** Linear Model ***

Call: lm(formula = LogCu ~ I5.ind + Bend.ind + Wemme.ind, data =
  STATS091028...CompDiss, na.action = na.exclude)
Residuals:
  Min      1Q  Median      3Q     Max

```

-0.3858 -0.1106 0.002999 0.05849 0.4843

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.6362	0.0735	8.6591	0.0000
I5.ind	0.5783	0.1185	4.8814	0.0002
Bend.ind	0.0806	0.2204	0.3656	0.7194
Wemme.ind	-0.1509	0.1122	-1.3442	0.1976

Residual standard error: 0.2078 on 16 degrees of freedom

Multiple R-Squared: 0.6986

F-statistic: 12.36 on 3 and 16 degrees of freedom, the p-value is 0.0001945

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
I5.ind	1	1.504047	1.504047	34.82366	0.0000223
Bend.ind	1	0.019694	0.019694	0.45598	0.5091526
Wemme.ind	1	0.078044	0.078044	1.80698	0.1976211
Residuals	16	0.691046	0.043190		

This output shows no significant effect of any of the hydrologic variables on composite samples after accounting for their location.

Below is the model-building results for a predictive DISSOLVED Cu model using water quality parameters.

*** Stepwise Regression ***

*** Stepwise Model Comparisons ***

Start: AIC= 0.7773

LogCu ~ pH + LogCond + LogAlk + LogHardness + LogTSS + LogDOC

Single term deletions

Model:

LogCu ~ pH + LogCond + LogAlk + LogHardness + LogTSS + LogDOC

scale: 0.01653735

	Df	Sum of Sq	RSS	Cp
<none>			0.545733	0.777256
pH	1	0.085500	0.631232	0.829680
LogCond	1	0.000007	0.545739	0.744188
LogAlk	1	0.408351	0.954084	1.152532
LogHardness	1	0.042475	0.588208	0.786656
LogTSS	1	0.038384	0.584116	0.782565
LogDOC	1	1.506971	2.052703	2.251151

Step: AIC= 0.7442

LogCu ~ pH + LogAlk + LogHardness + LogTSS + LogDOC

Single term deletions

Model:

LogCu ~ pH + LogAlk + LogHardness + LogTSS + LogDOC

scale: 0.01653735

	Df	Sum of Sq	RSS	Cp
<none>			0.545739	0.744188
pH	1	0.089825	0.635564	0.800938
LogAlk	1	0.461036	1.006776	1.172149
LogHardness	1	0.080184	0.625923	0.791297
LogTSS	1	0.041571	0.587310	0.752684
LogDOC	1	1.595148	2.140887	2.306261

*** Linear Model ***

Call: lm(formula = LogCu ~ pH + LogAlk + LogHardness + LogTSS + LogDOC, data = STATS091028...Diss, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.2424	-0.05989	-0.0008963	0.07676	0.3026

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.9282	0.5114	1.8152	0.0783
pH	-0.1837	0.0777	-2.3656	0.0238
LogAlk	0.8125	0.1516	5.3594	0.0000
LogHardness	-0.1986	0.0889	-2.2351	0.0321
LogTSS	0.0916	0.0569	1.6093	0.1168
LogDOC	0.6544	0.0656	9.9689	0.0000

Residual standard error: 0.1267 on 34 degrees of freedom

Multiple R-Squared: 0.8859

F-statistic: 52.77 on 5 and 34 degrees of freedom, the p-value is 4.663e-015

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr (F)
pH	1	0.017844	0.017844	1.1117	0.2991534
LogAlk	1	2.506984	2.506984	156.1871	0.0000000
LogHardness	1	0.083412	0.083412	5.1966	0.0290260
LogTSS	1	0.032061	0.032061	1.9974	0.1666574
LogDOC	1	1.595148	1.595148	99.3790	0.0000000
Residuals	34	0.545739	0.016051		

Important correlations are as follows:

Definitely Significant: DOC (+) > Alkalinity (+)

Significant: pH (-) > Hardness (-)

Questionable significance: TSS (+) -> $p=0.117 > 0.05$

Below is the Correlation matrix for WQ parameters with Cu in all measured dissolved samples.

*** Correlations for data in: STATS091028...Diss ***

	LogCu	LogDOC	LogTSS	LogHardness	LogAlk	LogCond
LogCu	1.00000000	0.87235734	0.23405853	0.4357839	0.6749536	0.3689499
LogDOC	0.87235734	1.00000000	0.11813486	0.3403690	0.4715702	0.2384475
LogTSS	0.23405853	0.11813486	1.00000000	0.4359164	0.2238464	0.2228422
LogHardness	0.43578390	0.34036904	0.43591642	1.00000000	0.7064009	0.8324036
LogAlk	0.67495362	0.47157017	0.22384641	0.7064009	1.00000000	0.6828413
LogCond	0.36894992	0.23844752	0.22284219	0.8324036	0.6828413	1.00000000
pH	0.06109058	0.02895802	-0.08825452	0.1522432	0.4473318	0.1366475

	pH
LogCu	0.06109058
LogDOC	0.02895802
LogTSS	-0.08825452
LogHardness	0.15224322
LogAlk	0.44733181
LogCond	0.13664750
pH	1.00000000

Therefore, the strongest correlations with dissolved Cu are DOC (0.872) and Alkalinity (0.675).

Below is the results for analyzing whether DOC or Alkalinity still has an effect on Cu in dissolved samples after the effect of Total Cu has been accounted for.

*** Linear Model ***

Call: lm(formula = LogCu ~ LogTotCu + LogAlk + LogDOC, data =
STATS091028...CuStats2,
na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.358	-0.04666	0.01221	0.065	0.242

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-0.2360	0.0750	-3.1468	0.0032
LogTotCu	0.4270	0.0803	5.3176	0.0000
LogAlk	0.1812	0.0997	1.8185	0.0769
LogDOC	0.5125	0.0653	7.8481	0.0000

Residual standard error: 0.1135 on 38 degrees of freedom

Multiple R-Squared: 0.8998

F-statistic: 113.8 on 3 and 38 degrees of freedom, the p-value is 0
28 observations deleted due to missing values

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
LogTotCu	1	3.546153	3.546153	275.3741	0.00000000
LogAlk	1	0.057410	0.057410	4.4581	0.04136938
LogDOC	1	0.793175	0.793175	61.5934	0.00000000
Residuals	38	0.489348	0.012878		

*** Linear Model ***

Call: lm(formula = LogCu ~ LogTotCu + LogDOC + LogAlk, data =
STATS091028...CuStats2,
na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.358	-0.04666	0.01221	0.065	0.242

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-0.2360	0.0750	-3.1468	0.0032
LogTotCu	0.4270	0.0803	5.3176	0.0000
LogDOC	0.5125	0.0653	7.8481	0.0000
LogAlk	0.1812	0.0997	1.8185	0.0769

Residual standard error: 0.1135 on 38 degrees of freedom

Multiple R-Squared: 0.8998

F-statistic: 113.8 on 3 and 38 degrees of freedom, the p-value is 0
28 observations deleted due to missing values

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
LogTotCu	1	3.546153	3.546153	275.3741	0.00000000
LogDOC	1	0.808000	0.808000	62.7447	0.00000000
LogAlk	1	0.042584	0.042584	3.3068	0.07688124
Residuals	38	0.489348	0.012878		

*** Linear Model ***

Call: lm(formula = LogCu ~ LogTotCu + LogAlk, data = STATS091028...CuStats2,
na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.4427	-0.1047	0.04144	0.1278	0.2612

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-0.2367	0.1199	-1.9746	0.0554
LogTotCu	0.7625	0.1086	7.0200	0.0000
LogAlk	0.2103	0.1591	1.3213	0.1941

Residual standard error: 0.1813 on 39 degrees of freedom

Multiple R-Squared: 0.7375

F-statistic: 54.79 on 2 and 39 degrees of freedom, the p-value is 4.705e-012
28 observations deleted due to missing values

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
LogTotCu	1	3.546153	3.546153	107.8343	0.0000000
LogAlk	1	0.057410	0.057410	1.7458	0.1941104
Residuals	39	1.282523	0.032885		

Yes, DOC still has a significant effect on the presence of Cu in dissolved samples. There is no significant effect of alkalinity (p=0.19) on dissolved Cu after total Cu has been accounted for.

Below is the model-building results for a predictive TOTAL Cu model using water quality parameters (Hardness, TSS, and DOC).

*** Stepwise Regression ***

*** Stepwise Model Comparisons ***

Start: AIC= 1.8908

LogCu ~ LogHardness + LogTSS + LogDOC

Single term deletions

Model:

LogCu ~ LogHardness + LogTSS + LogDOC

scale: 0.04297283

	Df	Sum of Sq	RSS	Cp
<none>			1.547022	1.890805
LogHardness	1	0.002005	1.549027	1.806864
LogTSS	1	0.848402	2.395423	2.653260
LogDOC	1	1.495364	3.042386	3.300223

Step: AIC= 1.8069

LogCu ~ LogTSS + LogDOC

Single term deletions

Model:

LogCu ~ LogTSS + LogDOC

scale: 0.04297283

	Df	Sum of Sq	RSS	Cp
<none>			1.549027	1.806864
LogTSS	1	1.180281	2.729308	2.901199
LogDOC	1	1.687014	3.236041	3.407933

Single term additions

Model:

LogCu ~ LogTSS + LogDOC

scale: 0.04297283

	Df	Sum of Sq	RSS	Cp
<none>			1.549027	1.806864
LogHardness	1	0.002005168	1.547022	1.890805

*** Linear Model ***

Call: lm(formula = LogCu ~ LogTSS + LogDOC, data = STATS091028...Tot, na.action =

na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.5018	-0.1028	-0.002281	0.09106	0.5244

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.0036	0.1476	0.0246	0.9805
LogTSS	0.4349	0.0819	5.3096	0.0000
LogDOC	0.5807	0.0915	6.3479	0.0000

Residual standard error: 0.2046 on 37 degrees of freedom

Multiple R-Squared: 0.677

F-statistic: 38.77 on 2 and 37 degrees of freedom, the p-value is 8.346e-010

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
LogTSS	1	1.558977	1.558977	37.23767	4.565006e-007
LogDOC	1	1.687014	1.687014	40.29596	2.125562e-007
Residuals	37	1.549027	0.041866		

Important correlations are as follows:

Definitely Significant: DOC (+) > TSS (+)

Below is the Correlation matrix for WQ parameters with Cu in all measured dissolved samples.

*** Correlations for data in: STATS091028...Tot ***

	LogCu	LogDOC	LogTSS	LogHardness
LogCu	1.0000000	0.6563562	0.5701968	0.4611405
LogDOC	0.6563562	1.0000000	0.1181349	0.3219472
LogTSS	0.5701968	0.1181349	1.0000000	0.5044135
LogHardness	0.4611405	0.3219472	0.5044135	1.0000000

Therefore, the strongest correlations with dissolved Cu are DOC (0.656) and TSS (0.570).

Below is the analysis of Cu and DOC throughout the course of a storm – looking at the flow-weighted samples from some of the Dixon Outfall storms. First Cu vs V/Vtot is examined, then DOC vs V/Vtot.

*** Linear Model ***

Call: lm(formula = LogCu ~ V.Vtot, data = STATS091028...Flow, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.52	-0.1598	-0.08293	0.1366	0.7177

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.9108	0.1009	9.0273	0.0000
V.Vtot	-0.6008	0.1713	-3.5064	0.0014

Residual standard error: 0.2984 on 31 degrees of freedom

Multiple R-Squared: 0.284

F-statistic: 12.29 on 1 and 31 degrees of freedom, the p-value is 0.001409

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
V.Vtot	1	1.094571	1.094571	12.29457	0.001408807
Residuals	31	2.759894	0.089029		

*** Linear Model ***

Call: lm(formula = LogDOC ~ V.Vtot, data = STATS091028...Flow, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.4354	-0.2109	-0.02955	0.1996	0.5806

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.8502	0.0888	9.5758	0.0000
V.Vtot	-0.5816	0.1508	-3.8570	0.0005

Residual standard error: 0.2626 on 31 degrees of freedom

Multiple R-Squared: 0.3243

F-statistic: 14.88 on 1 and 31 degrees of freedom, the p-value is 0.0005427

Analysis of Variance Table

Response: LogDOC

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
V.Vtot	1	1.025829	1.025829	14.87638	0.0005427125
Residuals	31	2.137665	0.068957		

*** Linear Model ***

Call: lm(formula = LogCu ~ LogDOC + V.Vtot, data = STATS091028...Flow, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.495	-0.09022	0.04409	0.1303	0.3676

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	0.2067	0.1397	1.4796	0.1494
LogDOC	0.8280	0.1421	5.8288	0.0000
V.Vtot	-0.1192	0.1451	-0.8214	0.4179

Residual standard error: 0.2077 on 30 degrees of freedom

Multiple R-Squared: 0.6642

F-statistic: 29.67 on 2 and 30 degrees of freedom, the p-value is 7.773e-008

Analysis of Variance Table

Response: LogCu

Terms added sequentially (first to last)

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
LogDOC	1	2.531151	2.531151	58.67275	0.0000000
V.Vtot	1	0.029109	0.029109	0.67475	0.4178792
Residuals	30	1.294205	0.043140		

The above sets of output suggest that, both Cu and DOC values decrease over the course of a storm

A.6 COMPOSITE STATISTICS

Analysis of Variance Models** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogCu ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	1.674504	0.718946
Deg. of Freedom	3	18

Residual standard error: 0.1998536
Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	1.674504	0.5581680	13.97465	0.00005991871
Residuals	18	0.718946	0.0399414		

95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method

critical point: 2.1009000000000002

response variable: LogCu

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.198	0.158	-0.13400	0.5300	
Bend-I-5	-0.380	0.167	-0.73200	-0.0289	****
Bend-Wemme	0.346	0.160	0.00968	0.6830	****
Dixon-I-5	-0.578	0.114	-0.81800	-0.3390	****
Dixon-Wemme	0.148	0.103	-0.06910	0.3660	
I-5-Wemme	0.727	0.117	0.48100	0.9720	****

Appears to be significant differences in Cutot concentrations between I5 and all other sites, and between Bend and Wemme.

Lgands
log LIGANDS

*** Analysis of Variance Model ***

Short Output:

Call:

aov(formula = logL ~ Site, data = X10uMStats, na.action = na.exclude)

Terms:

	Site	Residuals
Sum of Squares	0.2088314	0.5679475
Deg. of Freedom	3	15

Residual standard error: 0.1945846

2 observations deleted due to missing values

Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	0.2088314	0.06961048	1.838475	0.1834906
Residuals	15	0.5679475	0.03786317		

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1314

response variable: logL

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound
Bend-Dixon	0.1060	0.154	-0.2220	0.4330
Bend-I5	-0.0969	0.169	-0.4560	0.2620
Bend-Wemme	0.1950	0.163	-0.1520	0.5420
Dixon-I5	-0.2030	0.119	-0.4560	0.0515
Dixon-Wemme	0.0893	0.111	-0.1470	0.3260
I5-Wemme	0.2920	0.131	0.0136	0.5700 ****

Appears to be significant differences in Ligand concentrations between I5 and Wemme.

lgK

*** Analysis of Variance Model ***

Short Output:

Call:

aov(formula = logK ~ Site, data = X10uMStats, na.action = na.exclude)

Terms:

	Site	Residuals
Sum of Squares	3.448158	6.215737
Deg. of Freedom	3	14

Residual standard error: 0.6663191

3 observations deleted due to missing values

Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	3.448158	1.149386	2.588817	0.09432543
Residuals	14	6.215737	0.443981		

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1448

response variable: logK

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound
Bend-Dixon	-0.917	0.527	-2.050	0.212
Bend-I5	0.177	0.608	-1.130	1.480
Bend-Wemme	-0.296	0.557	-1.490	0.900
Dixon-I5	1.090	0.451	0.127	2.060 ****
Dixon-Wemme	0.622	0.380	-0.193	1.440
I5-Wemme	-0.473	0.487	-1.520	0.571

Appears to be significant differences in K-CuL between I5 and Dixon.

Cfree

*** Analysis of Variance Model ***

Short Output:

Call:

aov(formula = logCufree ~ Site, data = Model.vs.Exp, na.action = na.exclude)

Terms:

	Site	Residuals
Sum of Squares	48.59906	17.85262
Deg. of Freedom	3	16

Residual standard error: 1.056309

Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	48.59906	16.19969	14.5186	0.00007903105
Residuals	16	17.85262	1.11579		

95 % non-simultaneous confidence intervals for specified linear combinations, by the Fisher LSD method

critical point: 2.1199

response variable: logCufree

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.925	0.835	-0.845	2.700	
Bend-I5	-3.190	0.915	-5.130	-1.250	****
Bend-Wemme	0.488	0.862	-1.340	2.320	
Dixon-I5	-4.110	0.647	-5.480	-2.740	****
Dixon-Wemme	-0.437	0.570	-1.650	0.773	
I5-Wemme	3.670	0.682	2.230	5.120	****

Appears to be significant differences in Cufree concentrations between I5 and all other sites.

Alkalinity

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogAlk ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	0.8183919	0.5338832
Deg. of Freedom	3	18

Residual standard error: 0.1722213
Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	0.8183919	0.2727973	9.197427	0.0006591279
Residuals	18	0.5338832	0.0296602		

95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method

critical point: 2.1009
response variable: LogAlk

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.2150	0.1360	-0.0713	0.5010	
Bend-I-5	-0.2730	0.1440	-0.5760	0.0297	
Bend-Wemme	0.1570	0.1380	-0.1330	0.4470	
Dixon-I-5	-0.4880	0.0982	-0.6940	-0.2810	****
Dixon-Wemme	-0.0577	0.0891	-0.2450	0.1300	
I-5-Wemme	0.4300	0.1010	0.2180	0.6420	****

Appears to be significant differences in alkalinity between I5 and Wemme and I-5 and Dixon.

Hrdness

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogHardness ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	1.615319	0.254814
Deg. of Freedom	3	14

Residual standard error: 0.1349111
4 observations deleted due to missing values
Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	1.615319	0.5384398	29.58299	2.570929e-006
Residuals	14	0.254814	0.0182010		

95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method

critical point: 2.1448
response variable: LogHardness

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.750	0.1070	0.5210	0.9790	****
Bend-I-5	0.151	0.1130	-0.0907	0.3930	
Bend-Wemme	0.584	0.1230	0.3200	0.8480	****
Dixon-I-5	-0.599	0.0769	-0.7640	-0.4340	****
Dixon-Wemme	-0.166	0.0913	-0.3620	0.0301	
I-5-Wemme	0.433	0.0985	0.2210	0.6440	****

**Appears to be significant differences in hardness between I5 and Wemme, I-5 and
Dixon, Bend and Dixon, and Bend and Wemme.**

DC

*** Analysis of Variance Model ***

Short Output:

Call:

```
aov(formula = LogDOC ~ Site, data = STATS091028...CompDiss, na.action =
na.exclude)
```

Terms:

	Site	Residuals
Sum of Squares	0.6699371	0.7085800
Deg. of Freedom	3	18

Residual standard error: 0.1984075
Estimated effects may be unbalanced

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
Site	3	0.6699371	0.2233124	5.672786	0.006465129
Residuals	18	0.7085800	0.0393656		

95 % non-simultaneous confidence intervals for specified
linear combinations, by the Fisher LSD method

critical point: 2.1009
response variable: LogDOC

intervals excluding 0 are flagged by '****'

	Estimate	Std.Error	Lower Bound	Upper Bound	
Bend-Dixon	0.150	0.157	-0.1790	0.4800	
Bend-I-5	-0.148	0.166	-0.4970	0.2010	
Bend-Wemme	0.318	0.159	-0.0160	0.6520	
Dixon-I-5	-0.298	0.113	-0.5360	-0.0604	****
Dixon-Wemme	0.168	0.103	-0.0476	0.3840	
I-5-Wemme	0.466	0.116	0.2220	0.7100	****

Appears to be significant differences in DOC between I5 and Wemme, and I-5 and Dixon.

A.6.1 Paired t-Tests

A.6.1.1 10 μ M SA vs 2 μ M SA Tests

L10 vs L2

Paired t-Test

```
data: x: L10 in X10uM.vs.2uM , and y: L2 in X10uM.vs.2uM
t = -3.7639, df = 4, p-value = 0.0197
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
-325.21382 -49.10218
sample estimates:
mean of x - y
-187.158
```

Mean ligand concentration determined at 10 μ M SA is 187.2 nM less than the ligand concentration determined at 2 μ M (49.1 to 325.2nM, 95%CI).

K10 vs K2

Paired t-Test

data: x: logK10 in X10uM.vs.2uM , and y: logK2 in X10uM.vs.2uM
t = 6.2261, df = 3, p-value = 0.0084
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
0.5585153 1.7264847
sample estimates:
mean of x - y
1.1425

Mean conditional stability constants determined at 10uM SA are 1.1 log units stronger than constants determined at 2uM (0.6 to 1.7 log units, 95%CI).

A.6.1.2 Modeled Cufree Concentrations vs Experimental

SHM

Paired t-Test

data: x: SHM.Cufree in SHM , and y: logCufree in SHM
t = 2.9903, df = 19, p-value = 0.0075
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
0.3291906 1.8649502
sample estimates:
mean of x - y
1.09707

Mean free copper concentration calculated by SHM is 1.1 log units higher than actual concentrations (0.33 to 1.86 log units, 95%CI).

Gaussian

Paired t-Test

data: x: G.Cufree in Gaussian , and y: logCufree in Gaussian
t = 9.247, df = 19, p-value = 0
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
2.619679 4.152543
sample estimates:
mean of x - y
3.386111

Mean free copper concentration calculated by Gaussian DOM model is 3.39 log units higher than actual concentrations (2.62 to 4.15 log units, 95%CI).

NICA

Paired t-Test

data: x: ND.Cufree in NICA , and y: logCufree in NICA
t = 3.7459, df = 19, p-value = 0.0014
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
0.6061475 2.1413117
sample estimates:
mean of x - y
1.37373

Mean free copper concentration calculated by the NICA-Donnan DOM model is 1.37 log units higher than actual concentrations (0.61 to 2.14 log units, 95%CI).

A.6.2 Other t-Tests

Bend (3) vs Wemme (4) CuTot

Welch Modified Two-Sample t-Test

data: x: LogCu with Site = Bend , and y: LogCu with Site = Wemme
t = 2.6806, df = 1.4516814649241221, p-value = 0.1602
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-0.4683204 1.1609882
sample estimates:
mean of x mean of y
2.031283 1.684949

(INSIGNIFICANT)

I5 (1) vs Bend (3) (Cutot)

Welch Modified Two-Sample t-Test

data: x: LogCu with Site = Bend , and y: LogCu with Site = I-5
t = -3.0133, df = 1.3226930265858172, p-value = 0.1526
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-1.2997432 0.5392642
sample estimates:
mean of x mean of y
2.031283 2.411523

(INSIGNIFICANT)

I5 (1) vs Wemme (4) CuTot

Welch Modified Two-Sample t-Test

data: x: LogCu with Site = I-5 , and y: LogCu with Site = Wemme
t = 10.2681, df = 9.9778049885117035, p-value = 0
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
0.5688617 0.8842851
sample estimates:
mean of x mean of y
2.411523 1.684949

Median dissolved copper concentration at I-5 is 5.3 times higher than at Wemme (3.7 to 7.7 fold, 95%CI).

I5 (1) vs Wemme (4) Ligands

Welch Modified Two-Sample t-Test

data: x: logL with SiteNum = 1 , and y: logL with SiteNum = 4
t = 1.8834, df = 6.976473980885312, p-value = 0.1018
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-0.07480899 0.65844744
sample estimates:
mean of x mean of y
2.245437 1.953618

(INSIGNIFICANT)

I5 (1) vs Dixon (2) Cutot

Welch Modified Two-Sample t-Test

data: x: LogCu with Site = Dixon , and y: LogCu with Site = I-5
t = -5.3834, df = 9.6480853724751867, p-value = 0.0003
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-0.8188854 -0.3377784
sample estimates:
mean of x mean of y
1.833191 2.411523

Median dissolved copper concentration at I-5 is 3.8 times higher than at Dixon Outfall (2.2 to 6.6 fold, 95%CI).

I5 vs Dixon (CuFREE)

Welch Modified Two-Sample t-Test

data: x: logCufree with Site = Dixon , and y: logCufree with Site = I5
t = -4.0519, df = 3.28971163034866, p-value = 0.0227
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-7.185665 -1.037332
sample estimates:
mean of x mean of y
-12.195 -8.083501

Mean free copper concentration at I-5 is 4.1 log units higher than at Dixon Outfall (1.0 to 7.2 log units, 95%CI).

I5 (1) vs Wemme (4) Cufree

Welch Modified Two-Sample t-Test

data: x: logCufree with SiteNum = 1 , and y: logCufree with SiteNum = 3
t = 3.3444, df = 3.5527422923508607, p-value = 0.0344
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
0.4756851 7.0193149
sample estimates:
mean of x mean of y
-8.1775 -11.925

Mean free copper concentration at I-5 is 3.7 log units higher than at Wemme (0.5 to 7.0 log units, 95%CI).

I5 (1) vs Bend (3) Cufree

Welch Modified Two-Sample t-Test

data: x: logCufree with SiteNum = 1 , and y: logCufree with SiteNum = 3
t = 2.9597, df = 3.8057746730213009, p-value = 0.0442
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
0.1361209 6.2368764
sample estimates:
mean of x mean of y
-8.083501 -11.27

Mean free copper concentration at I-5 is 3.2 log units higher than at Bend (0.1 to 6.2 log units, 95%CI).

I5 (1) vs Dixon logK

Welch Modified Two-Sample t-Test

```

data: x: logK with SiteNum = 1 , and y: logK with SiteNum = 2
t = -3.7131, df = 3.2656098628248924, p-value = 0.0294
alternative hypothesis: difference in means is not equal to 0
95 percent confidence interval:
-1.9523665 -0.1943002
sample estimates:
mean of x mean of y
11.59333 12.66667

```

Two of the Dixon Stability constants used in this comparison may not be accurate, so the significance between I-5 and Dixon stability constants is in question.

A.6.3 Linear Regression Models

logCutot vs logDOC

*** Linear Model ***

```

Call: lm(formula = LogCu ~ LogDOC, data = STATS091028...CompDiss, na.action =
na.exclude)

```

Residuals:

Min	1Q	Median	3Q	Max
-0.3348	-0.1079	-0.008873	0.1055	0.3595

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.2411	0.1013	12.2463	0.0000
LogDOC	1.1275	0.1525	7.3954	0.0000

Residual standard error: 0.179 on 20 degrees of freedom

Multiple R-Squared: 0.7322

F-statistic: 54.69 on 1 and 20 degrees of freedom, the p-value is 3.84e-007

There is a correlation with dissolved copper and dissolved organic carbon concentration.

logCutot vs logHardness

*** Linear Model ***

```

Call: lm(formula = LogCu ~ LogHardness, data = STATS091028...CompDiss,
na.action = na.exclude)

```

Residuals:

Min	1Q	Median	3Q	Max
-0.4383	-0.1698	-0.03054	0.1993	0.495

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.1515	0.2347	4.9065	0.0002
LogHardness	0.7086	0.1924	3.6833	0.0020

Residual standard error: 0.2631 on 16 degrees of freedom

Multiple R-Squared: 0.4589

F-statistic: 13.57 on 1 and 16 degrees of freedom, the p-value is 0.002012

4 observations deleted due to missing values

There is a correlation with dissolved copper concentration and hardness.

logCutot vs logAlkalinity

*** Linear Model ***

```

Call: lm(formula = LogCu ~ LogAlk, data = STATS091028...CompDiss, na.action =

```

na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.4758	-0.1247	-0.06523	0.1724	0.5282

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.0735	0.2050	5.2356	0.0000
LogAlk	0.9278	0.2132	4.3513	0.0003

Residual standard error: 0.2479 on 20 degrees of freedom

Multiple R-Squared: 0.4863

F-statistic: 18.93 on 1 and 20 degrees of freedom, the p-value is 0.0003095

There is a correlation with dissolved copper and alkalinity.

logL10 vs logDOC

*** Linear Model ***

Call: lm(formula = logL ~ logDOC, data = X10uMStats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.2662	-0.1287	0.02001	0.1254	0.3113

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.7495	0.1078	16.2299	0.0000
logDOC	0.5193	0.1615	3.2167	0.0051

Residual standard error: 0.1685 on 17 degrees of freedom

Multiple R-Squared: 0.3784

F-statistic: 10.35 on 1 and 17 degrees of freedom, the p-value is 0.005063

2 observations deleted due to missing values

There is a correlation with ligand concentration and DOC.

logL10 vs logHardness

*** Linear Model ***

Call: lm(formula = logL ~ logHardness, data = X10uMStats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.2869	-0.1499	0.03471	0.1039	0.3568

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.8420	0.1800	10.2318	0.0000
logHardness	0.2021	0.1538	1.3140	0.2086

Residual standard error: 0.1916 on 15 degrees of freedom

Multiple R-Squared: 0.1032

F-statistic: 1.726 on 1 and 15 degrees of freedom, the p-value is 0.2086

4 observations deleted due to missing values

(INSIGNIFICANT)

logL10 vs Alkalinity

*** Linear Model ***

Call: lm(formula = logL ~ logAlkalinity, data = X10uMStats, na.action = na.exclude)

Residuals:

Min 1Q Median 3Q Max
-0.3003 -0.1393 0.04074 0.09637 0.3073

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.6685	0.1668	10.0042	0.0000
logAlkalinity	0.4518	0.1802	2.5069	0.0226

Residual standard error: 0.1826 on 17 degrees of freedom

Multiple R-Squared: 0.2699

F-statistic: 6.285 on 1 and 17 degrees of freedom, the p-value is 0.02262
2 observations deleted due to missing values

There is a correlation with ligand concentration and alkalinity.

logCufree vs logDOC

*** Linear Model ***

Call: lm(formula = logCufree ~ logDOC, data = Model.vs.Exp, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.7435	-0.4752	-0.1158	0.4342	1.144

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-12.9557	0.3847	-33.6746	0.0000
logDOC	1.9386	0.6343	3.0562	0.0080

Residual standard error: 0.5876 on 15 degrees of freedom

Multiple R-Squared: 0.3837

F-statistic: 9.34 on 1 and 15 degrees of freedom, the p-value is 0.008002
3 observations deleted due to missing values

There is a correlation between free copper and dissolved organic carbon concentration.

*** Linear Model ***

Call: lm(formula = logCufree ~ logHardness, data = Model.vs.Exp, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.5845	-0.3191	-0.125	0.1629	1.116

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-13.8002	0.4869	-28.3446	0.0000
logHardness	1.6627	0.4427	3.7555	0.0027

Residual standard error: 0.4775 on 12 degrees of freedom

Multiple R-Squared: 0.5403

F-statistic: 14.1 on 1 and 12 degrees of freedom, the p-value is 0.002744
6 observations deleted due to missing values

There is a correlation between free copper concentration and hardness.

logCufree vs logCuTot

*** Linear Model ***

Call: lm(formula = logCufree ~ logCuTot, data = Model.vs.Exp, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.9401	-0.3349	-0.1056	0.3378	1.121

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-15.2932	1.0673	-14.3294	0.0000
logCuTot	1.8597	0.5738	3.2412	0.0055

Residual standard error: 0.574 on 15 degrees of freedom

Multiple R-Squared: 0.4119

F-statistic: 10.51 on 1 and 15 degrees of freedom, the p-value is 0.005481

3 observations deleted due to missing values

There is a correlation between free copper and dissolved copper.

logCufree vs Alkalinity

*** Linear Model ***

Call: lm(formula = logCufree ~ logAlkalinity, data = Model.vs.Exp, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-1.425	-0.8586	-0.2291	0.7071	2.158

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	-16.9884	1.0286	-16.5167	0.0000
logAlkalinity	6.4813	1.1069	5.8556	0.0000

Residual standard error: 1.127 on 18 degrees of freedom

Multiple R-Squared: 0.6558

F-statistic: 34.29 on 1 and 18 degrees of freedom, the p-value is 0.00001517

There is a correlation between free copper and alkalinity.

logK10 vs log DOC

*** Linear Model ***

Call: lm(formula = logK ~ logDOC, data = X10uMStats, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-1.655	-0.3541	-0.0576	0.4123	1.337

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	12.8436	0.4863	26.4086	0.0000
logDOC	-1.0157	0.7528	-1.3493	0.1960

Residual standard error: 0.7364 on 16 degrees of freedom

Multiple R-Squared: 0.1022

F-statistic: 1.821 on 1 and 16 degrees of freedom, the p-value is 0.196

3 observations deleted due to missing values

(INSIGNIFICANT)

LogK10 vs logAlkalinity

*** Linear Model ***

Call: lm(formula = logK ~ logAlkalinity, data = X10uMStats, na.action = na.exclude)

Residuals:
Min 1Q Median 3Q Max
-1.171 -0.2656 -0.0798 0.2153 1.137

Coefficients:
Value Std. Error t value Pr(>|t|)
(Intercept) 14.3309 0.5201 27.5526 0.0000
logAlkalinity -2.4021 0.5769 -4.1640 0.0007

Residual standard error: 0.5384 on 16 degrees of freedom
Multiple R-Squared: 0.5201
F-statistic: 17.34 on 1 and 16 degrees of freedom, the p-value is 0.0007316
3 observations deleted due to missing values

There is a correlation between the calculated conditional stability constant and alkalinity.

Log10 vs logHardness

*** Linear Model ***

Call: lm(formula = logK ~ logHardness, data = X10uMStats, na.action = na.exclude)

Residuals:
Min 1Q Median 3Q Max
-0.7087 -0.2939 -0.0731 0.3704 0.785

Coefficients:
Value Std. Error t value Pr(>|t|)
(Intercept) 13.9269 0.4370 31.8705 0.0000
logHardness -1.3954 0.3805 -3.6672 0.0025

Residual standard error: 0.4539 on 14 degrees of freedom
Multiple R-Squared: 0.4899
F-statistic: 13.45 on 1 and 14 degrees of freedom, the p-value is 0.002537
5 observations deleted due to missing values

There is a correlation between the calculated conditional stability constant and hardness.

Alkalinity vs Hardness

*** Linear Model ***

Call: lm(formula = LogAlk ~ LogHardness, data = STATS091028...CompDiss, na.action = na.exclude)

Residuals:
Min 1Q Median 3Q Max
-0.3443 -0.09597 0.05272 0.122 0.271

Coefficients:
Value Std. Error t value Pr(>|t|)
(Intercept) 0.1551 0.1609 0.9640 0.3494
LogHardness 0.6408 0.1319 4.8577 0.0002

Residual standard error: 0.1804 on 16 degrees of freedom
Multiple R-Squared: 0.5959
F-statistic: 23.6 on 1 and 16 degrees of freedom, the p-value is 0.0001746
4 observations deleted due to missing values

There is a correlation between alkalinity and hardness.

A.6.4 Intra Storm Samples

Below is the summary of the one-sample t-test comparing Ligand concentrations between FF and composite samples on a particular day. For this reason, it is a one-sample t-test; I assume there is dependence between the FF and composite samples for a particular storm. What's quantified here is the difference b/w the 2 values.

One-sample t-Test

```
data: D.L in FF.Comp.Speciation.Summary
t = 2.9108, df = 7, p-value = 0.0226
alternative hypothesis: mean is not equal to 0
95 percent confidence interval:
 25.12649 242.67351
sample estimates:
mean of x
 133.9
```

One-sample t-Test

```
data: D.LogL in FF.Comp.Speciation.Summary
t = 2.7489, df = 7, p-value = 0.0286
alternative hypothesis: mean is not equal to 0
95 percent confidence interval:
 0.03564474 0.47436309
sample estimates:
mean of x
 0.2550039
```

Therefore, with no transformations, FF samples have [L] that's 133.9 nM higher than their composite samples (25.1 – 243, 95% CI). This is significant (p = 0.0226).
Considering the log-transformation, FF samples average [L] 1.8 times higher than their composite samples (1.09 – 2.98, 95% CI). This is significant (p = 0.0286).

Paired t-Test

```
data: x: Lff in STATS.FF.Composite.Comparison , and y: Lcomp in
STATS.FF.Composite.Comparison
t = 2.934, df = 7, p-value = 0.0219
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
 27.59075 256.77425
sample estimates:
mean of x - y
 142.1825
```

Paired t-Test

```
data: x: logLff in STATS.FF.Composite.Comparison , and y: logLcomp in
STATS.FF.Composite.Comparison
t = 2.8078, df = 7, p-value = 0.0262
alternative hypothesis: mean of differences is not equal to 0
95 percent confidence interval:
 0.04152703 0.48469452
sample estimates:
mean of x - y
 0.2631108
```

Below is the summary of the [L] vs DOC association

*** Linear Model ***

Call: lm(formula = .L. ~ DOC, data =
Speciation.Summary...Dixon.Outfall...STATS,
na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-194.5	-37.25	-2.837	48.53	144.1

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	14.6830	23.7205	0.6190	0.5420
DOC	13.7094	1.6788	8.1662	0.0000

Residual standard error: 75.39 on 23 degrees of freedom

Multiple R-Squared: 0.7436

F-statistic: 66.69 on 1 and 23 degrees of freedom, the p-value is 3.009e-008

*** Linear Model ***

Call: lm(formula = log.L. ~ LogDOC, data =
Speciation.Summary...Dixon.Outfall...STATS, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.6969	-0.08464	0.08434	0.2046	0.4301

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.4381	0.1664	8.6414	0.0000
LogDOC	0.6871	0.1730	3.9713	0.0006

Residual standard error: 0.3236 on 23 degrees of freedom

Multiple R-Squared: 0.4068

F-statistic: 15.77 on 1 and 23 degrees of freedom, the p-value is 0.0006041

Therefore, with no transformations, [L] is significantly ($p < 0.0001$) positively associated with DOC. On average, a unit (1 mg/L) increase in DOC is associated with an increase in [L] of 13.7 nM (10.2 – 17.2, 95% CI).

Considering the log-transformation, [L] is significantly ($p = 0.0006$) positively associated with DOC. On average, a doubling in DOC is associated with a 1.61-fold increase in [L] (1.26 – 2.06, 95% CI).

Below is the summary of the [L] vs Hardness association. We didn't examine the untransformed [L]-Hardness association because it looks to violate the equal variance assumption.

*** Linear Model ***

Call: lm(formula = log.L. ~ LogHard, data =
Speciation.Summary...Dixon.Outfall...STATS, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.6865	-0.1634	0.05888	0.2686	0.4934

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.2614	0.2507	5.0322	0.0000
LogHard	0.6783	0.2079	3.2620	0.0034

Residual standard error: 0.3474 on 23 degrees of freedom

Multiple R-Squared: 0.3163

F-statistic: 10.64 on 1 and 23 degrees of freedom, the p-value is 0.003429

Considering the log-transformation, [L] is significantly ($p=0.0034$) positively associated with Hardness. On average, a doubling in Hardness is associated with a 1.60-fold increase in [L] (1.19 – 2.16, 95% CI).

Below is the summary of the [L] vs Alkalinity association. I didn't examine the untransformed [L]-Alkalinity association because it looks to violate the equal variance assumption.

*** Linear Model ***

Call: lm(formula = log.L. ~ LogAlk, data =
Speciation.Summary...Dixon.Outfall...STATS, na.action = na.exclude)

Residuals:

Min	1Q	Median	3Q	Max
-0.9082	-0.1732	0.1009	0.1809	0.6115

Coefficients:

	Value	Std. Error	t value	Pr(> t)
(Intercept)	1.4856	0.3624	4.0996	0.0004
LogAlk	0.6256	0.3939	1.5881	0.1259

Residual standard error: 0.3988 on 23 degrees of freedom

Multiple R-Squared: 0.09882

F-statistic: 2.522 on 1 and 23 degrees of freedom, the p-value is 0.1259

Considering the log-transformation, [L] is NOT significantly associated with Alkalinity (p>0.05).

