PHASE I: PRELIMINARY ENVIRONMENTAL INVESTIGATION OF HEAVY METALS IN HIGHWAY RUNOFF

Final Report

by

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16. ABSTRACT

Heavy metals in highway runoff continue to be a national concern for most transportation agencies including the Washington State Department of Transportation (WSDOT). In this project, a comprehensive critical review of the literature and data associated with heavy metals in stormwater runoff from highway settings was conducted to assist WSDOT in better understanding the indicators associated with elevated concentrations in response to suggestions that locations for dissolved metals treatment BMPs are to be determined based solely on Average Annual Daily Traffic.

Results found that multiple regression models have been used to predict contaminant concentrations with some success, however there are still considerable uncertainties related to the predictions due to the complexity and variability of highway settings. Furthermore, studies indicate that multiple linear regression models are only applicable in the geographic region and range of conditions represented by the original data set. Regional data necessary to populate and substantiate such a model for the State of Washington do not currently exist. As such, additional runoff quality and ancillary information across a variety of Washington highway AADT settings would be needed to improve the reliability associated with locating BMPs for treating metals contamination. In discussing these uncertainties with WSDOT and the department of Ecology, it was determined that a multiple regression model was not feasible.

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EXECUTIVE SUMMARY

Heavy metals such as cadmium, copper, lead and zinc in highway runoff continue to be a national concern for most transportation agencies including the Washington State Department of Transportation (WSDOT). In this project, a comprehensive critical review of the literature and data associated with heavy metals in stormwater runoff from highway settings was conducted to assist WSDOT in better understanding the indicators associated with elevated concentrations in response to directives from the Washington State Department of Ecology that locations for dissolved metals treatment BMPs are to be determined based solely on Average Annual Daily Traffic (AADT). Specific consideration was given to soluble copper and soluble zinc as these compounds are of most concern to the WSDOT.

Based on information available, the study concluded that:

- AADT is not, by itself, a reliable estimator for dissolved metals concentrations.

Metals concentrations are only correlated to AADT in conjunction with numerous other factors. For example, event mean concentrations of dissolved copper and zinc were found to decrease with higher total event rainfall and seasonal cumulative precipitation, and to increase with respect to duration of the antecedent dry period and AADT. Additionally, surrounding land use, vegetation, soil characteristics, pervious versus impervious area, and rainfall intensity all contributed to the severity of contaminant loadings.

Multiple regression models have been used to predict contaminant concentrations with some success, however there are still considerable uncertainties related to the predictions due to the complexity and variability of highway settings. Furthermore, studies indicate that multiple linear regression models are only applicable in the geographic region and range of conditions represented by the original data set. Regional data necessary to populate and substantiate such a model for the State of Washington do not currently exist. As such, additional runoff quality and ancillary information across a variety of Washington highway AADT settings would be needed to improve the reliability associated with locating BMPs for treating metals contamination. In discussing these uncertainties with WSDOT and the department of Ecology, it was determined that a multiple regression model was not feasible.

As alternatives to regression, several ideas were discussed:

- Study timing of fish presence and first-flush runoff
- Dilution models requiring receiving water monitoring
- Refine existing guidance for natural dispersion and infiltration
- Determine infiltration and treatment afforded by unlined conveyances not designed for infiltration or pollutant removal.

PHASE I: PRELIMINARY ENVIRONMENTAL INVESTIGATION OF HEAVY METALS IN HIGHWAY RUNOFF

1.0 INTRODUCTION

1.1 Need for Investigation

Heavy metals come from a variety of anthropogenic and natural sources. The Federal Highway Administration (FHWA) identifies cadmium, chromium, copper, iron, lead, nickel, and zinc as the metals typically associated with highway runoff, declaring that heavy metals are one of the most common contaminants in highway runoff (FHWA 1999). The U.S. Environmental Protection Agency (U.S. EPA) states that the primary sources of these metals are caused by wear and tear of various vehicle components such as tires, engine parts, brake pads; auto body rusting; lubricants; and fuel combustion (U.S. EPA, 1995). Citing U.S. EPA and FHWA sources as well as Ball et. al. (1998), Table 1 presents the sources of metals from highway operations as summarized by the East-West Gateway Coordinating Council (2000) and Granato 2003a. A review of the literature pertaining to metal sources is provided by Granato et al. (2003a). Some of this information is based on historic data from the 1980s and early 1990s and therefore may not adequately reflect updated information from today. For example, since 1973 EPA began working to phase out lead in gasoline products (U.S. EPA, 1996). As a result, studies have shown a dramatic decrease in lead concentrations in highway runoff. However, lead is still being deposited on highway surfaces through other sources such as paints used on the right of ways, through atmospheric deposition, tires, and automotive lead-acid batteries (FHWA, 1999 and RMA).

These metals accumulate on roadways during dry periods, and are washed off from roadway surfaces during rainfall runoff events. Existing and pending state and federal regulations require significant reductions in toxic metals pollution from stormwater runoff including drainage from highways and bridge decks. The Washington State Department of Transportation (WSDOT) is currently looking for a way to address these concerns in a cost-effective manner in order to maximize environmental benefit with finite financial resources. In order to accomplish this goal, it is necessary to determine which sites require enhanced treatment for metals. The Washington State Department of Ecology (Ecology) requires enhanced metals treatment best management practices (BMPs) for roadways solely using thresholds based on annual average daily traffic

(AADT) loading (Ecology, 2004, 2005). However, studies by several investigators have indicated that pollutant loadings in highway runoff were not dependent solely on AADT, and that use of AADT alone is not predictive (Driscoll et al., 1990; CH2M Hill, 1998; Kayhanian et al., 2003).

Table 1. Sources of Metals in Highway Runoff

Pollutant	Source
Cadmium	Tire wear, lubricants, and insecticide application
Chromium	Metal plating, moving engine parts and brake lining wear
Copper	Metal plating, bearing and bushing wear, moving engine parts, brake lining wear, deicers, fungicides and insecticides
Iron	Auto body rust, steel highway structures such as bridges and guardrails, brake lining wear, deicers, and moving engine parts
Lead	Leaded gasoline from auto exhaust, tire wear, lubricating oil and grease, bearing wear and atmospheric deposition
Manganese	Moving engine parts and fuel additive
Nickel	Diesel fuel and gasoline, lubricating oil, deicers, metal plating, bushing wear, brake lining wear and asphalt paving
Zinc	Tire wear, brakes, motor oil and grease

Given the economic impact of instituting enhanced metals treatment BMPs across the state of Washington, it is pertinent and prudent to investigate methodologies for improving the predictability of dissolved metals concentrations. While a number of dissolved metals are important, of particular interest because of their ubiquity in highway runoff environments are dissolved copper and dissolved zinc.

In natural streams and stormwater runoff, metals may be present in both dissolved and particulate forms. Dissolved metal is operationally defined as that metal which passes through a 0.45-micron (μm) filter (U.S. EPA 1994 and 1996). Washington's WAC 173-201a expresses freshwater quality criteria for these metals as dissolved rather than total (Appendix A). In addition, many of the metals criteria are expressed as functions of hardness in WAC 173-201a. Both acute and chronic metals criteria for cadmium, copper, lead, nickel, and zinc are expressed as functions of hardness. As hardness increases, so does the allowable concentration of the metals, as shown in Appendix A. This occurs because the primary cationic components of hardness (calcium and magnesium) are non-toxic and can be readily absorbed by living organisms in direct competition with dissolved heavy metals. Therefore, as hardness increases,

the bioavailability and, thus, toxicity of a given concentration of a particular metal decreases (HydroQual, 2003). Because of its role in determining the water quality standards for these metals, hardness could be a significant factor in determining when enhanced treatment may be required.

1.2 Objectives

The long-term goal is to develop an improved, scientifically defensible methodology for predicting highway runoff water quality. At this juncture, the effort is limited to predicting copper and zinc concentrations in highway runoff. Given the evolving complex body of literature concerning metals and the relatively localized scale in which the results appear to be applicable, this goal will be divided into two phases. The intent of Phase I is to improve understanding of the degree to which existing models and guidance accurately predict total and dissolved metal concentrations and when enhanced metals treatment is needed; alternatively, to assess the uncertainty in predictive models and guidance. This will enable an assessment of the adequacy of current agency interpretation of existing models and stormwater management guidance with regard to enhanced metals treatment, and to provide information needed for decision-making for future direction in this regard. Researchers were to investigate and analyze previous studies and data sets associated with highway runoff and prepare an interim report to a Technical Advisory Committee. Phase II, if conducted, would be based on the Technical Advisory Committee's review of the interim report's findings and recommendations on how to proceed with Phase II of the investigation by determining whether or not there are other avenues of current research that would be beneficial in WSDOT's efforts to improve the predictability of dissolved metals concentrations. This interim report has been prepared to document the work completed with respect to the Phase I tasks.

There were nine specific Phase I objectives identified during the scoping portion of this project. In Phase I, research was undertaken to address the following:

1. Conduct a literature review of methods and data used for estimating metals concentration in highway runoff.

   Outcome: Assurance that all relevant data are being considered

2. Obtain existing raw data – expected to be mostly from California and Washington – regarding highway runoff quality, quantity, causative variables, and sampling locations.

Outcome: Assurance that all applicable data are available for analysis

3. Evaluate existing data to determine if a robust correction factor for converting event mean concentrations to peak hourly concentrations can be found, in order to include existing WSDOT data in analysis.

Outcome: Maximize use of existing data if defensible

4. Assess watershed characteristics related to significant runoff pollutant factors.

Outcome: Assessment of variables necessary to predict enhanced metals triggers

5. Reevaluate information from California Department of Transportation (Caltrans), WSDOT, and any other applicable data sets obtained subsequent to the literature review, to confirm or refute current interpretation by State of Washington and determine if other inferences can be made from data sets. Evaluation should include contacting Caltrans personnel who conducted the ADT study (Kayhanian et. al., 2003) and those who wrote the Discharge Characterization Study (Caltrans, 2003), in order to reconcile differences in conclusions regarding ADT and highway runoff pollutants. Consider the effects of representativeness, unbalanced sample sizes, collinearity, psuedoreplication, missing data (systematic or random), and autocorrelation in data. Determine whether more predictive algorithms/equations can be developed when looking only at dissolved copper and zinc.

   Outcome: Assessment of validity of in-use enhanced metals trigger, and assessment of data for use in further analysis

6. Identify gaps in highway runoff water quality data sets containing concomitant measurement of potential explanatory variables; e.g. urban/non-urban, finer land-use categories, ADT, TSS, local climatic data (quarter-hourly precipitation, antecedent dry period, etc.), etc.

   Outcome: Data needs assessment for a scientifically defensible enhanced treatment trigger algorithm/equation

7. Assess the nature of the data needed for filling the gaps in terms of missing variable data, kinds of samples required, sample size, site representativeness, and cost and effort of additional collection.

   Outcome: Experimental design requirements in order to fill data gaps identified in the data gap assessment

8. If feasible, (i.e., if data gaps are not present) develop statistical multiple regression equations for better enhanced treatment triggers for Western Washington.

Outcome: Either a new enhanced metals trigger that is acceptable to Ecology, or a finding that available data are not adequate to define a scientifically defensible trigger

9. Report findings to a Technical Advisory Committee including staffs from WSDOT and Ecology.

Outcome: A more complete understanding of:

- *Interpretation and application of existing studies*
- *Experimental needs to fill in data gaps*
- *Costs of further work*
- *Other directions that could be taken to address dissolved metals in highway stormwater runoff (e.g., treatment thresholds, treatment options, etc.)*

2.0 REVIEW OF SCIENTIFIC LITERATURE

A literature review was performed to identify relevant studies and data addressing the nature of metals concentrations in highway runoff and the factors affecting metals concentrations, particularly dissolved metals concentrations. Emphasis was placed on dissolved metals studies and data, because dissolved metals are the regulated metals fraction in Washington. Databases consulted included National Technical Information Service, Environmental Sciences and Pollution Management (through CSA Illumina which provides access to more than 100 full-text and bibliographic databases), and the Washington State University Library catalog. In addition, an Internet search was conducted using Google (http://google.com) and Google Scholar (http://scholar.google.com) search engines to identify technical reports not published in formal journal articles or books. Keywords used included "highway, runoff, and metals." The United States Geological Survey (USGS) in cooperation with the FHWA compiled an online database of citations and abstracts for literature relevant to the study of highway and urban runoff water quality spanning the 1970's through 1990's (http://ri.water.usgs.gov/fhwa/biblio/default.htm). Additional sources for information included a WSU science library search, the Caltrans Division of Environmental Analysis (http://www.dot.ca.gov/hq/env/stormwater/), the WSDOT Stormwater Research Reports (http://www.wsdot.wa.gov/environment/stormwater/sw_reports.htm), and WSU-conducted research.

2.1 Dissolved versus Total Metals Concentrations

The differentiation between dissolved and total metals represents a challenge in interpreting and comparing studies. Meybeck and Helmer (1989) studied the ratio of dissolved to total metals concentrations in natural fresh water systems. In their study, partitioning between dissolved and particulate phases was dependent on the solubility of the metal. However, many different factors influence the ratio of dissolved to total metals. Important factors include water temperature, pH, hardness, concentrations and physical and chemical characteristics (e.g., particle size distribution, cation exchange capacity) of particles with metal binding sites, concentrations of competing cations, particulate organic carbon, dissolved organic carbon, and

presence of anions, e.g. chloride, sulfide and phosphate, that can form low-solubility precipitates with metal cations.

Granato et al. (2003a) acknowledge that paved surfaces are fundamentally different both physically and chemically than natural waterways with much higher percentages of some metals being found in the dissolved phase. As illustrated in Table 2 and Figure 1, with the exception of lead and manganese, Breault and Granato (2000) reported the fraction of dissolved metals in highway runoff varied considerably across study sites. The dissolved copper fraction ranged from 30% to 100%[1] of total, and the dissolved zinc fraction ranged from 14% to 90% of total. Data from sites evaluated statewide in California from 2000-2003 had the particulate fraction of zinc range from 60-70% (30-40% dissolved) and the particulate fraction of copper range from 50-55% (45-50% dissolved). Although data from sites evaluated in Washington is limited, one study from 2003-2005 also shows variability in dissolved fractions for copper and zinc. This data is summarized in Figure 2.

[1] (Dupuis and others, 1985), from Breault and Granato (2000). 100% under very low flow snowmelt conditions with very low suspended solids

Table 2. Hierarchy of the Relative Fraction of Trace Metals in the Dissolved Fraction

(after Breault and Granato, 2000)

Highway Runoff Study	Relative Dissolved Fraction of Metal
Laxen and Harrison (1977)	Cd > Zn > Pb
Gupta et al. (1981)	Zn > Pb
Ellis and Revitt (1982)	Cd > Zn = Cu > Pb
Morrison et al. (1984)	Zn > Cd > Cu > Pb
Yousef et al. (1984)	Ni > Zn > Cu > Cd > Cr > Pb
Dupuis et al. (1985)	Cu > Cd = Ni > Cr > Zn > Pb
Harrison and Wilson (1985)	Cd > Cu > Pb
Yousef et al. (1985)	Cd ≈ Cu > Cr > Zn ≈ Ni > Pb
Morrison et al. (1987)	Cd > Zn > Cu > Pb
Revitt and Morrison (1987)	Cd ≈ Zn > Cu > Pb
Schiffer (1989)	Ni ≈ Zn > Cu > Pb
Morrison et al. (1990)	Cd > Zn > Cu > Pb
Morrison and Florence (1990)	Cd > Zn > Cu > Pb
Revitt et al (1990)	Cu > Zn > Cd > Pb
Legret et al. (1995)	Zn > Ni > Cd > Cu > Cr > Pb
Sansalone et al. (1995)	Cr > Cd > Cu ≈ Zn > Pb
Marsalek et al. (1997)	Ni ≈ Zn > Cu
Sansalone and Buchberger (1997)	Zn > Cu > Cd > Pb
Speiran (1998)	Zn > Cu > Pb
Legret and Paggoto (1999)	Zn ≈ Cu > Cd > Pb

The percent dissolved of each constituent's total concentration decreases from left to right, the greater than symbol (>) indicates a difference of at least 10 percent between adjacent constituents;
≈, a difference that is less than 10 percent.
Cd, Cadmium; Cr, Chromium; Cu, Copper; Ni, nickel; Pb, lead; Zn zinc

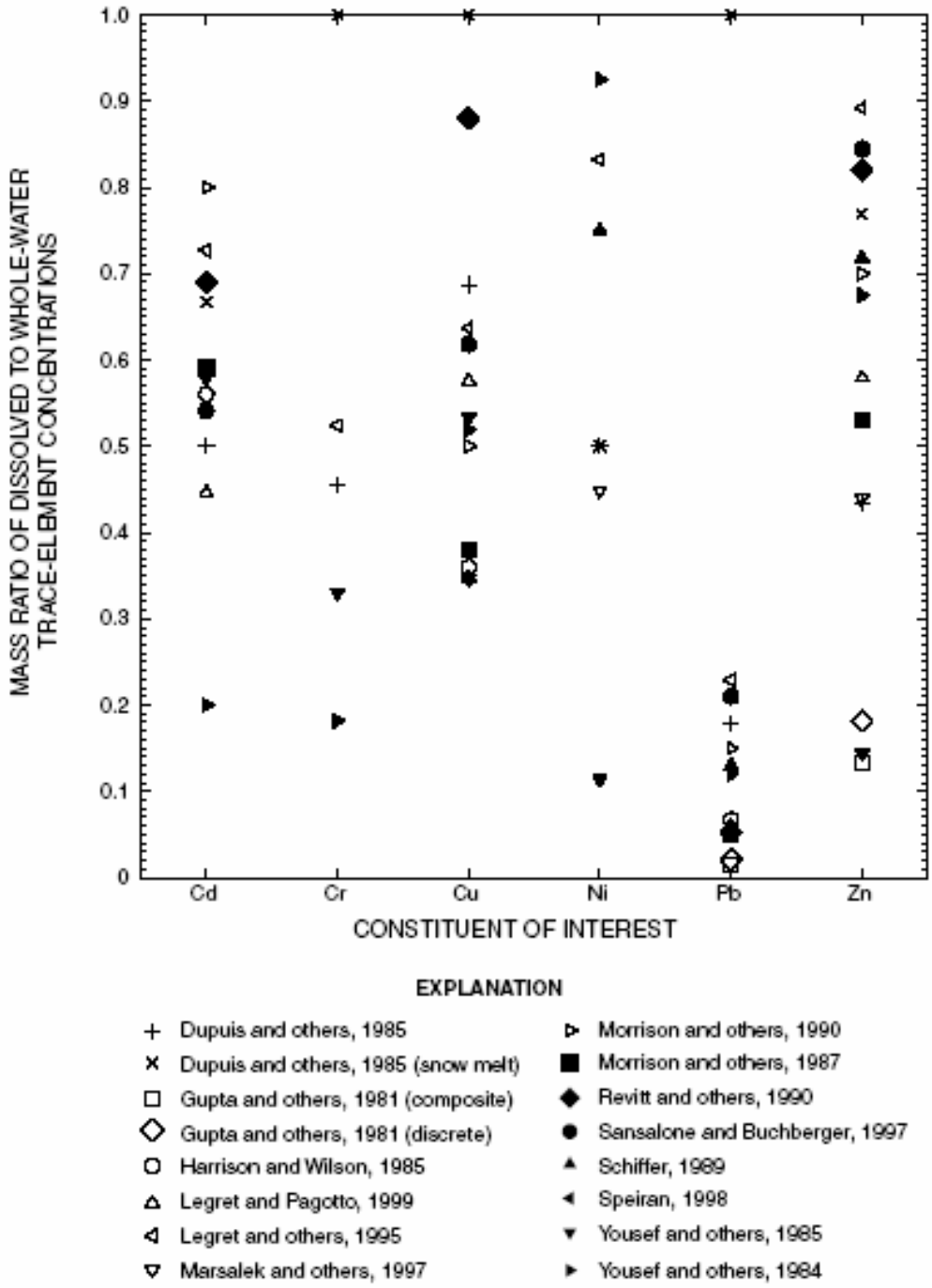


Figure 1. Dissolved Fraction of Metals in Highway Runoff
(after Breault and Granato, 2000)

Because determining dissolved fractions requires additional processing steps prior to preserving the samples and because the dissolved fraction has been of regulatory concern mainly since the early 1990's, many studies, especially earlier ones, have focused on reporting total metals. In addition, traditional sample and analysis practices implemented prior to the mid-1990's could have resulted in contaminated samples, artificially elevating metals concentration results. Recent implementation of clean sampling techniques (e.g. EPA Method 1669) and analytical methods (e.g., EPA Methods 200.8 and 1631) have improved the validity of trace metals results. If any trace-element data collected today is not supported by quality-assurance and quality-control (QA/QC) documentation to reveal the validity of the data, then it is accepted as suspect (Granato 2003a). It is therefore necessary to stratify highway runoff studies that distinguish between dissolved and total concentrations. If not specifically reported as dissolved in the study, it was assumed that any metal data represented total concentration.

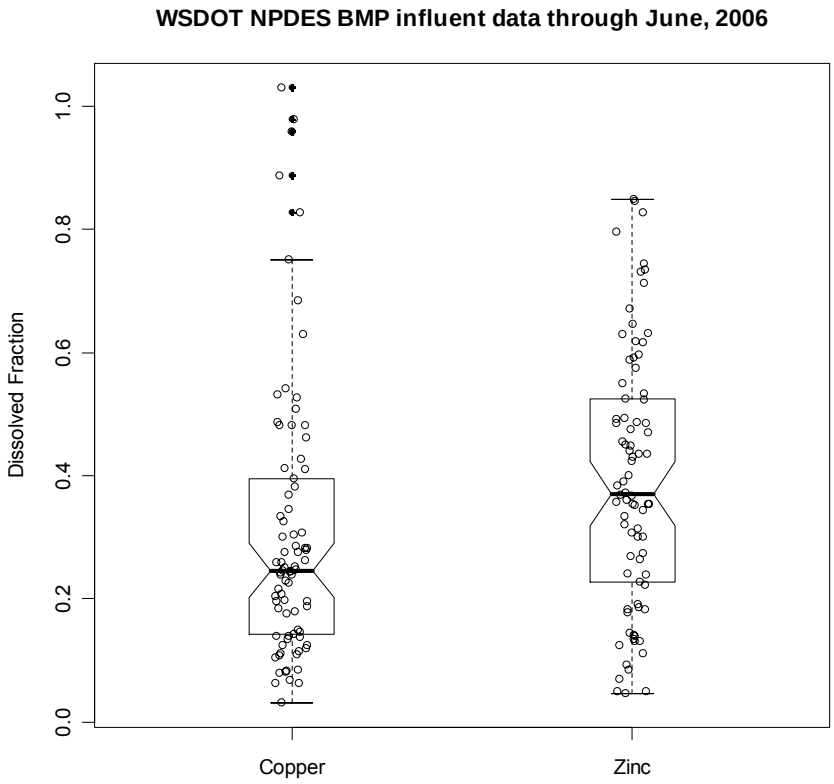


Figure 2: Washington highway data obtained from WSDOT National Pollutant Discharge Elimination System compiled and evaluated with respect to dissolved fractions of copper and zinc.

2.2 Factors Affecting Metals Concentrations in Highway Runoff

As early as 1972, when Professor Robert Sylvester published the Washington State Highway Department Research Report No. 7.1 titled *Character and Significance of Highway Runoff Waters,* attempts have been made to relate stormwater runoff quality to ADT (also referred to as annual average daily traffic (AADT)). The philosophy and attraction of such an approach are easy to understand. If metals in stormwater come from cars, the thought is that the more cars traveling over the roadway, the greater the metals concentrations should be. In addition to the apparent logic of the argument, such an approach results in an easy way to determine which highways should be subjected to stormwater regulations requiring metals removal. However, data from monitoring studies from around the country have revealed that the AADT-pollutant load relationship is considerably more complicated than originally envisioned.

In a study of runoff from an urban highway in Florida, McKenzie and Irwin (1983) found that zinc concentrations were higher at a medium traffic site (50,000 AADT) than from either a low traffic site (4,000 AADT) or high traffic site (70,000 AADT). Copper concentrations at all three sites were comparable.

Driscoll et al. (1990) indicated that pollutant loadings in highway runoff were not dependent on AADT alone. A statistically significant difference between the pollutant discharge of urban highways (AADT greater than 30,000 vehicles per day) and rural highways (AADT less than 30,000 vehicles per day) was found, and it was concluded that AADT should be used only as an indicator to distinguish between urban and rural highways. Other factors identified as influencing pollutants loading included vehicle turbulence, quantity of paved surface and vegetation types in relation to total drainage area of the right-of-way, and surrounding land use. Surrounding land use was identified as the most important general factor influencing levels of pollutants in highway runoff.

Miller (2005) also determined that although AADT was a factor, pollutant loadings in highway runoff were not dependent on AADT alone. There was an overall increase in pollutants with the increase of AADT; however, no direct relationship could be made between the two. Additionally, Miller found that the metals concentration decreased with increasing pavement age.

Irish et al. (1998) found copper concentrations in Austin, Texas to be highly influenced by volume of traffic during the storm. Conversely, zinc concentrations were found to be influenced

by traffic count during the antecedent dry period and the runoff characteristics of the preceding storm. Specific model parameters identified as significantly affecting copper and zinc concentrations were:

- *Copper* – Total duration of storm, total volume of flow per unit area of watershed during storm, and average number of vehicles traveling through the storm in a single lane.
- *Zinc* - Total duration of storm, total flow volume per unit area of watershed during storm, average number of vehicles during the antecedent dry period in a single lane, total duration of preceding storm, and total flow volume per unit area of watershed during the preceding storm event.

California Department of Transportation (Caltrans) studies (Kayhanian et al., 2003; Caltrans 2003) found no direct linear correlation between highway runoff pollutant event mean concentrations and AADT alone, in data collected from highways with AADT ranging from 1,800 to 259,000 based on untreated runoff from the pavement. However, through multiple regression analysis, it was shown that AADT in conjunction with factors associated with watershed characteristics and pollutant build-up and wash off has a statistically significant effect on most highway runoff constituent concentrations, including copper and zinc. Event mean concentrations of dissolved copper and zinc were found to decrease with higher total event rainfall and seasonal cumulative precipitation, and to increase with duration of the antecedent dry period and AADT (Caltrans 2003). Additional information regarding the Caltrans study is provided in Section 3.12.

In a first-flush study conducted in California, Kim et al. (2003) reported watershed area, antecedent dry days, storm duration, volume of total runoff, runoff coefficient, and average rainfall intensity, in addition to average daily traffic, could all be correlated to event mean concentration.

2.3 Significance of First-Flush Effects

The concept of first-flush is that the initial portion of runoff has the highest constituent concentrations in the runoff event and concentrations are diluted as the storm event progresses. In areas with a distinct seasonal rainfall pattern, the “seasonal” first-flush concept provides that

the initial runoff after an extended dry period contains higher mass load or concentration than that produced later in the precipitation season.

Because WAC 173-201a copper and zinc acute criteria are based on peak 1-hour average concentrations, first-flush effects represent another potential important concept that needs to be considered. Flint (2004) reported that at least three different definitions have been used to define first-flush:

1. Helsel et al. (1979) used:

   $M_*(t) \geq V_*(t)$

2. Urbonas and Stahre (1993) used:

   $M_*(t) \geq 0.8$ and $V_*(t) \leq 0.2$

3. Wanielista and Yousef (1993) used:

   $M_*(t) \geq 0.5$ and $V_*(t) \leq 0.25$

$M_*(t)$ and $V_*(t)$ represent the dimensionless normalized mass and flow volume, respectively. . While acknowledging several possible definitions for first-flush, WSDOT (2005a) defined the first-flush runoff as the discharge produced by the first 0.5 inch of precipitation or the 6-month storm event.

Evidence of both event and seasonal first-flush has been observed in data collected from California highways (Caltrans, 2003; Stenstrom and Kayhanian, 2005; Kim et al., 2003). Kim et al. (2003) concluded that most metals, including dissolved copper and zinc, exhibit first-flush characteristics on concentration and mass bases. The first-flush usually occurred in the first 30 percent of the total runoff volume. Several other researchers have similarly concluded that dissolved constituents in stormwater runoff almost always exhibit first-flush affects (Harrison and Wilson, 1985; Hewitt and Rashed, 1992; Sansalone and Buchberger, 1997).

In contrast, data collected at a Spokane, Washington wet detention pond exhibited first-flush characteristics for total metals for all but one winter storm event, but no first-flush was observed in the dissolved metals data (Yonge et al., 2002). A definitive seasonal first-flush event was observed for runoff following an extended antecedent dry period at a Vancouver, Washington wet detention pond during a June 1998 storm event, but no first-flush characteristics were

observed in subsequent storm events that had shorter antecedent dry periods. During the spring, summer, and fall, first-flush events were observed less consistently, occurring during some, but not all, storm events. When a first-flush occurred, the metals exhibiting the greatest first-flush phenomenon was in the order Pb>Zn>Cu>Cd. The lack of consistent first-flush characteristics in dissolved copper and zinc data collected in Washington leads to questions regarding the applicability of findings from studies conducted in California, which was found to exhibit first-flush characteristics for dissolved metals. However, one possible reason for these inconsistent first-flush characteristics in Washington could be the difference in the antecedent dry periods reported in the two studies. Nevertheless, data is not currently available to quantifiably know if this is the correct explanation.

One factor that may contribute to the dichotomy is the impact of watershed size. According to Characklis and Wiesner (1997) first-flushes in larger watersheds may result from a variety of first-flushes from smaller watersheds. As a result, this would broaden the concentration profile over time and inhibit the determination of exact first-flush effects.

3.0 EVALUATION OF DATA SETS

In a national report concerning the evaluation of water quality issues for highway planning, Bank et al. (1995) found that hard supporting data on highway runoff water quality impacts are generally not available and studies are based on extrapolative science and hypothecation. They concluded that quantification of nonpoint source pollution and water quality impacts are not typical activities within most highway planning and design procedures and as a consequence, actual data sets are scarce. The Transportation Research Board (1997) expressed a similar sentiment by concluding there were no established national formats for the exchange of key data sets generated by the highway water-quality research community. In cooperation with the FHWA, the USGS designed and implemented a National Highway Runoff Water Quality Data and Methodology Synthesis (NDAMS) project to help address these information needs (Granato et al., 2003b). In reviewing approximately 10% of the 2,600 reports contained in the NDAMS database, Granato (2003c) concluded that the lack of detailed metadata as well as technical issues related to the collection, processing and analysis of samples, raises concerns regarding the veracity of many data sets.

Washington Department of Ecology existing and proposed ADT thresholds for enhanced metals treatment BMPs, are based, in part, on review of data collected in California and Michigan. The monitoring results were evaluated to assess relationships between concentration and ADT. Based on the aforementioned wide range of dissolved metal concentrations reported in numerous studies, the applicability of these two studies with respect to runoff from Washington highways is limited.

3.1 Kayhanian Data

Kayhanian et al. (2003) completed a study titled, *The Impact of Annual Average Daily Traffic on Highway Runoff Pollutant Concentrations* to determine whether a correlation exists between AADT and the concentrations of highway runoff pollutants. Other factors, such as precipitation factors, antecedent conditions, and contributing drainage area, also were evaluated. The Kayhanian et al. (2003) study used data from 1997 to 2001 from sites representing a full range of physical parameters from seven out of the 12 Caltrans districts. The principal statistical methods applied to address the study objective consisted of multiple linear regression and analysis of

covariance. Thresholds for statistical significance were set at 95% ($p < 0.05$) for all analyses. Major findings from the Kayhanian et al. (2003) study include:

- Weak to no direct correlation between AADT and pollutant concentrations existed for all constituents evaluated (including dissolved copper and zinc), based on a simple linear regression analysis.
- AADT should only be used as one indicator instead of a sole predictor of pollutant concentrations.
- Event mean concentrations of dissolved copper and zinc were found to decrease with maximum rainfall intensity, seasonal cumulative precipitation, and drainage area, and to increase with respect to duration of the antecedent dry period and AADT. In addition, dissolved copper concentrations decreased with event rainfall amount.
- Contributing land use appears to significantly affect concentrations of many pollutants in highway runoff, though no statistically significant relationship was found for dissolved copper or zinc. The study recommended additional data collection and analysis to conclusively establish specific effects for different land uses.

3.2 Caltrans Data

Caltrans completed a *Discharge Characterization Study Report* (CTSW-RT-03-065.51.42, November 2003) that included an in-depth statistical analysis of the factors affecting runoff from transportation facilities. The objectives of the study included:

- identifying relationships between runoff quality and AADT, drainage area, precipitation factors, and antecedent conditions;
- updating multiple linear regression models of runoff quality produced from earlier data by Kayhanian et al. (2003); and
- determining whether there are significant differences in runoff quality from different geographic regions.

The Caltrans characterization study used data from 2000 to 2003 with an effort to capture a full range of hydrologic and antecedent conditions typical across California. The principal statistical methods applied to address the study objectives consisted of multiple linear regression, analysis of variance, and analysis of covariance. Thresholds for statistical significance were set

at 95% ($p < 0.05$) for all analyses. Statistical analysis procedures were reviewed by the University of California, Davis Statistics Laboratory. Dissolved copper and zinc were evaluated in this study.

The multiple linear regression model statistics that Caltrans utilized were designed for whole storm data (i.e., event mean concentrations (EMC)). An example of the multiple linear regression equation that Caltrans developed for dissolved copper can be seen below:

$$Ln(Cu_{dissolved}) = 2.919 - 0.290 * Ln(ER) + 0.185 * Ln(ADP) - 0.102 * CP^{1/3} + 3.679 * AADT * 10^{-6}$$

where Cu is dissolved copper [µg/L], ER is event rainfall, ADP is antecedent dry period, and CP is cumulative precipitation.

However, even with EMC data, the adjusted model R-squared value that they found for dissolved copper was only 0.508, while the dissolved zinc and dissolved lead values were only 0.316 and 0.076, respectively. Models using peak hourly data as required in the WAC would most likely have an even higher variability because of the use of non-averaged values. In addition, multiple linear regression equations are limited to the region/site from which the original data used to develop the model were collected. Table 3-9 in the Caltrans (2003) report contains more information on the multiple linear regression model statistics and coefficients.

Data qualities that can limit the ability to analyze and interpret the data, as identified by the Caltrans characterization study, include representativeness of sampling methods and data collection, psuedoreplication, collinearity of the predictor variables, and the overall data set size and quality. The following summarizes how each of these factors affects the findings regarding the relationship of dissolved copper and zinc concentrations in highway runoff to the variables evaluated:

- *Representativeness* – Data collected and analyzed must be representative of the range of conditions and concentrations occurring. The Caltrans characterization study used methods specific to collecting stormwater quality samples and are expected to be representative for California, particularly locales where most of the sampling was done.

- *Psuedoreplication* – Psuedoreplication occurs when a category is represented by a few sites sampled many times, leading to an inflated estimated significance of that category in statistical comparisons to other categories (e.g., comparison of data from a few rest areas to data collected from over 40 highway sites).

- *Collinearity* – Highly correlated variables can create difficulty in assessing the effects of a specific variable. The Caltrans characterization study evaluated collinearity and excluded highly correlated variables from the analysis.

- *Data Set Quality and Size* – Incomplete or censored data can limit the interpretation of statistical analysis. The Caltrans characterization study design collected data for a wide range of sites and environmental conditions, including 635 dissolved copper and zinc samples at 46 sites.

Major findings from the Caltrans characterization study for dissolved copper and zinc include:

- Event mean concentrations of dissolved copper and zinc were found to decrease with higher total event rainfall and seasonal cumulative precipitation, and to increase with respect to duration of the antecedent dry period and AADT. These factors were found to be interrelated. No one factor alone was found to be predictive.

- Dissolved copper and zinc concentrations were significantly higher in urban transportation areas (with higher traffic concentrations), compared to agricultural, commercial, residential, and open land use areas.

- Dissolved copper concentrations exhibited variation by geographic region; however, dissolved zinc did not. Caution in interpreting geographic variation is warranted as some regions were represented by relatively fewer highway miles.

- The results are generally consistent with and provide qualitative validation of models developed and reported by Kayhanian et al. (2003).

- There are unaccounted for factors contributing to variability in runoff, such as aerial deposition.

3.3 WSDOT Data

Washington highway data obtained from WSDOT National Pollutant Discharge Elimination System (NPDES) Progress Reports (2004 and 2005b) at inlets to Best Management Practice (BMP) facilities (i.e., prior to treatment), and a floating bridge stormwater monitoring project (Herrera Environmental Consultants, 2005) were compiled and evaluated with respect to ADT. The floating bridge study evaluated concentrations of metals on the bridge deck and at the outlet of down spouts; data from only the three bridge deck stations are reported here. The WSDOT data are event mean concentrations; whereas the bridge deck data are from grab samples

collected during storm events. Table 3 summarizes the monitoring locations evaluated and the associated ADT. Note that these monitoring efforts occurred between late fall and early spring (i.e., the wet season). Consequently, pollutant concentrations in these samples may be different than concentrations of comparable samples taken at the same locations during dry season storms.

Figure 3 contains scatter plots of dissolved copper and zinc event mean concentration (EMC) data collected and reported in the annual NPDES progress reports. There is no apparent relationship between ADT and concentrations of these metals. Highest concentrations of both dissolved copper and zinc were observed at the 90,000 ADT level. When mean and median EMCs are considered, there still is no direct correlation between ADT and concentrations. Inclusion of data collected from three floating bridges in the Puget Sound area (Figure 4) illustrates an even more inconsistent relationship of dissolved copper and zinc concentrations to ADT, suggesting that other site-specific or environmental factors are affecting concentrations. A more robust analysis of the data against site-specific and environmental factors was not performed, however, due to the relatively small sample size and number of sites. (Again, it should be noted that these are not EMCs, but are from grab samples collected during storm events.)

Table 3. WSDOT Monitoring Locations Evaluated

Highway	ADT	Period Monitored	Number of Measurements
SR 121 (Tumwater)	5,000	12/9/04 – 3/20/05	6
Hood Canal Bridge – Deck	15,000 [a]	3/19/05 – 4/7/05	2
SR 525 MP 3.3 (Mukilteo)	30,000	1/17/05 – 4/7/05	5
SR 525 MP 4.1 (Mukilteo)	30,000	1/17/05 – 4/7/05	5
SR 5 at MP 96.2 (Tumwater)	90,000	11/17/03 – 3/20/05	17
SR 405 at MP 26	90,000	12/13/03 – 1/26/04	5
SR 405 at MP 29.5 (Bothell)	90,000	1/8/04 – 4/7/05	12
SR 520 Bridge – Bridge Deck	100,000 [a]	3/19/05 – 4/1/05	12
I-90 Bridge – Bridge Deck	125,000 [a]	3/26/05	2
SR 5 at MP 109	130,000	11/23/03 – 3/24/04	9
SR 5 at MP 188.1 (Everett)	160,000	12/5/03 – 5/26/04	12

[a] From 2004 Traffic Flow Map, 2004 Annual Traffic Report, Washington Department of Transportation <http://www.wsdot.wa.gov/mapsdata/tdo/PDF_and_ZIP_Files/Annual_Traffic_Report_2004.pdf>

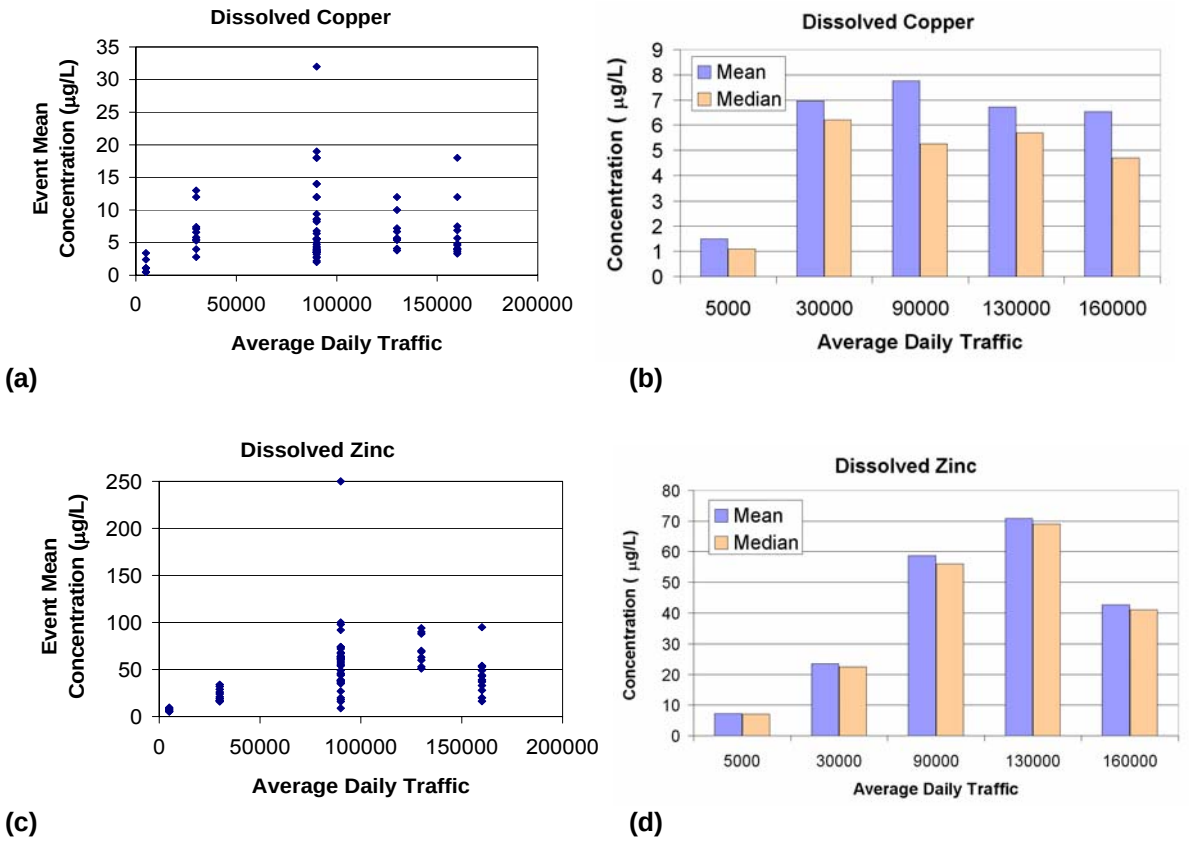


Figure 3. Dissolved copper and zinc versus average daily traffic for individual sample events (a and c) and overall mean and median concentrations (b and d) for data collected from November 2003 through May 2005 for WSDOT's NPDES program.

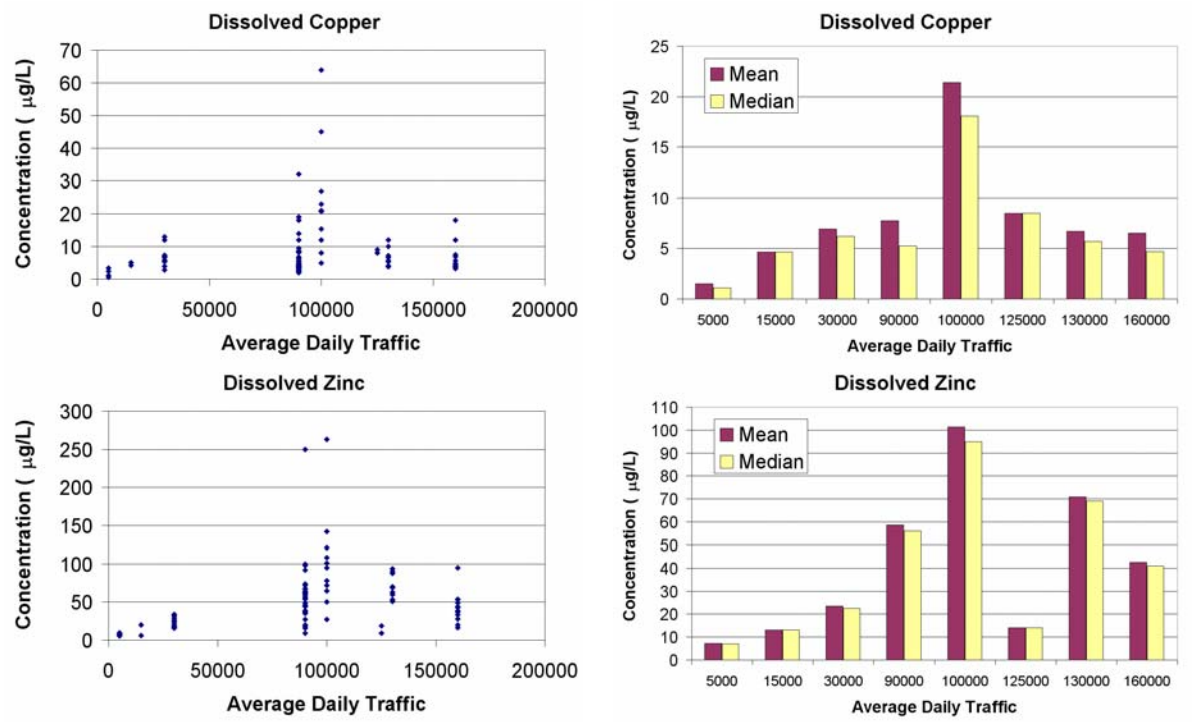


Figure 4. Dissolved copper and zinc versus average daily traffic for individual sample events (a and c) and overall mean and median concentrations (b and d) for data collected from November 2003 through May 2005 for WSDOT's NPDES program and Floating Bridge Study.

3.4 Washington State University Studies

Yonge et al. (2002) conducted a comprehensive study of highway runoff that included two locations in Washington (Spokane and Vancouver). A wet detention pond located at the intersection of US195 and Interstate 90 was studied at the Spokane site utilizing ISCO samplers to monitor inlet and outlet concentrations. Most of the flow at this site was direct highway runoff although a small amount of spring flow was intercepted by the pond. The study in Vancouver was at a dry pond off Interstate 5 near Burnt Bridge Creek. Samples were taken upstream and downstream of a detention pond again using ISCO samplers. Runoff at this site originated from an extensive drainage area which incorporated flows through many pervious and non-pervious areas (i.e., pipes and ditches). The National Cooperative Highway Research Program (NCHRP) sponsored study included a limited amount of hourly and event mean concentration (EMC) data for dissolved and total metals. Data from this study was analyzed as

part of this project to determine if enough information was available to establish a relationship between peak hourly concentration and EMC. However, the lack of a definitive first-flush pattern for dissolved metals made determining a robust, event-independent peaking factor impossible. It was concluded that significantly more data would be needed to quantify this relationship. The specific number of events needed would depend on the level of uncertainty acceptable in the final analysis.

3.5 Michigan Department of Transportation

A CH2M Hill (1998) study for the Michigan Department of Transportation produced the relationships shown in Figure 5. For sites located in Ann Arbor (41,000 ADT), Flint (51,000 ADT) and Grand Rapids (120,000 ADT), the nonlinear relationships are clearly demonstrated. Over the course of three years, one sample was collected per storm event. During these three years three different samples were collect from each site. While the general trend is upward, the cadmium concentration drops over 30% as the ADT rises between Ann Arbor and Flint. The downward blip shown in zinc concentration at Flint further demonstrates the difficulty relating metals directly to ADT.

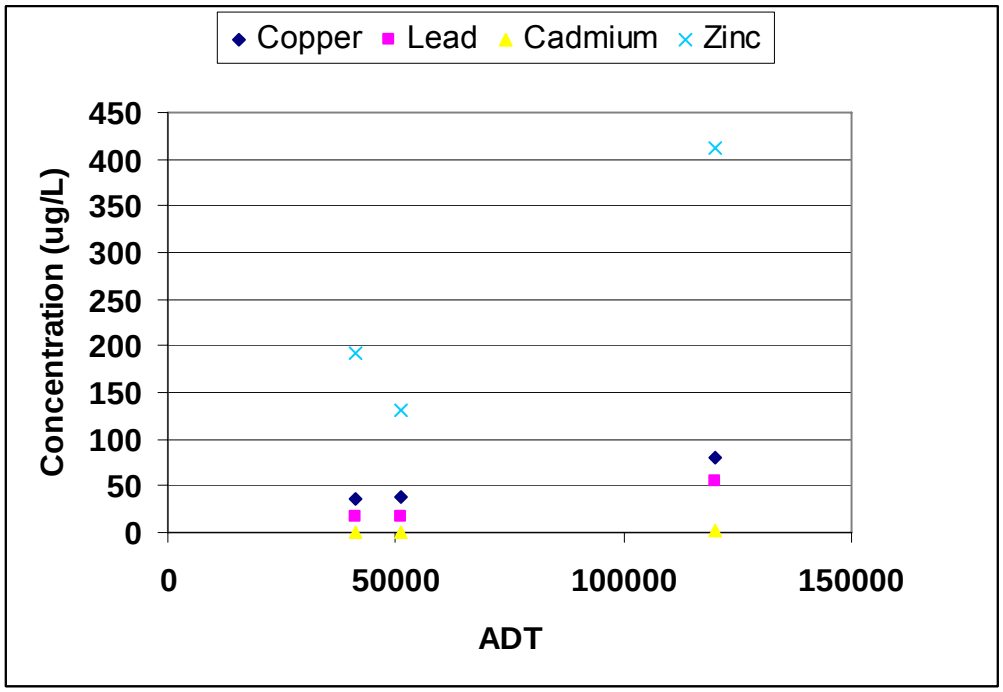


Figure 5. Total Recoverable Metals versus Average Daily Traffic in Michigan DOT Study

4.0 MULTIPLE REGRESSION EQUATIONS FOR ENHANCED TREATMENT TRIGGERS

Various statistical models may be used to examine the correlation between dissolved metals and known or suspected factors including, but not limited to, ADT, watershed area, wind, relative humidity, antecedent dry days, storm duration, total rainfall volume, runoff coefficient, average rainfall intensity, and adjacent land use. The simplest model would consist of a linear multivariate expression in the general form of:

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_N X_N$$

where α is a constant, β represents regression coefficients describing the amount of dependent variable change for a unit change of the related factor X.

A regression model represents the average relationship between a dependent variable (e.g., event mean concentration) and independent variables (e.g., ADT, antecedent dry period), and may be useful in identifying causative factors affecting stormwater quality (Irish et al., 1998). Regression models are generally limited to the region or site from which the original data used to develop the model were collected and tend to be unreliable when applied to conditions beyond the range of the original data set (Driscoll et al., 1990). In addition, Kayhanian et al. (2003) made this point for their results.

Analysis of data collected from California highways statewide over a multi-year period found that multiple linear regression (MLR) analysis is useful in identifying the environmental and site-specific factors that affect runoff quality and, thus is useful for directing future management and monitoring activities. However, MLR models for that study accounted for less than 50% of the variability of most constituent concentrations in runoff and may not be adequate to predict concentrations at specific sites or for specific rainfall events. Expanded use of statistical methods, such as exploration of transformations of predictor variables, analysis of covariance, and principal components analysis may only marginally improve the predictive ability of the MLR models (Caltrans, 2003).

Given that current data gaps are significant and include missing explanatory variables that would preclude comprehensive analysis; and given that to be useful, models should only be applied to the regions from which they were developed, with data inputs within the ranges used to develop the models; no statistical correlations were performed for this research report.

5.0 DATA GAPS AND NEEDS IN HIGHWAY RUNOFF WATER QUALITY INFORMATION

Based on a thorough review of the literature, significant data gaps exist with regard to the causal effects of variables leading to elevated concentrations of dissolved metals in highway environments. The most significant factors influencing dissolved metals concentrations for any area are identified in Table 4, based on the literature review of factors affecting highway runoff quality. These gaps can be further divided into "edge of pavement factors" and "outlet to stream factors" which is significant when addressing where the compliance point will be. Edge of Pavement factors include AADT, precipitation volume, rainfall intensity, flow rate, storm duration, pavement type, pavement age, antecedent dry period, first-flush impacts, atmospheric deposition, wind, and highway characteristics related to traffic movement. Outlet to Stream factors include land use, vegetation type, watershed area, soil types, highway shoulder characteristics, time to outlet, infiltration rates, potential non-highway runoff sources, receiving stream quantity and quality, and existing BMP performance.

Many of the studies reported in the literature fail to either report or monitor the processes in sufficient detail to allow comprehensive analysis of the data. Moreover, many of the studies are limited in scope such that spatial variability cannot be adequately addressed. However, given the general conclusion that monitoring results are only valid regionally, transferring results from other locations would likely produce significant errors even if more thorough investigations could be conducted.

Acknowledging the potential for regional discrepancies, it is somewhat difficult to precisely develop and propose a sampling plan that would definitively answer the question "When are enhanced metals treatment BMPs needed?" To begin to answer this question brings up the concept of uncertainty in a regulatory environment. The multiple linear regression equation developed in the Caltrans study still has a relatively large error band associated with the predictions.

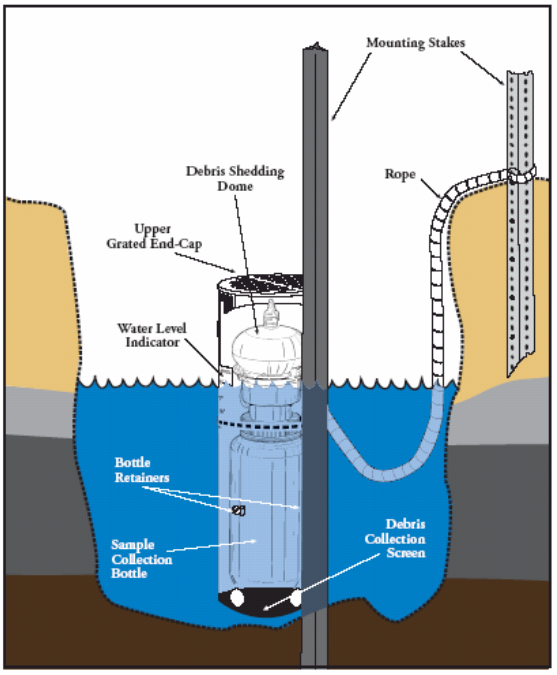
In addition, given the current lack of low AADT runoff-quality data for Washington, a sampling matrix sufficient to uniquely identify the contributions from each of the factors shown in Table 4 would result in a tremendous number of locations and samples. Consequently, it was not deemed feasible to tackle all components in Phase 2 of this study. Instead, we propose a

reconnaissance level investigation to examine the most probable parameters and help determine if developing a statically valid trigger for requiring metals reducing BMPs would be practicable.

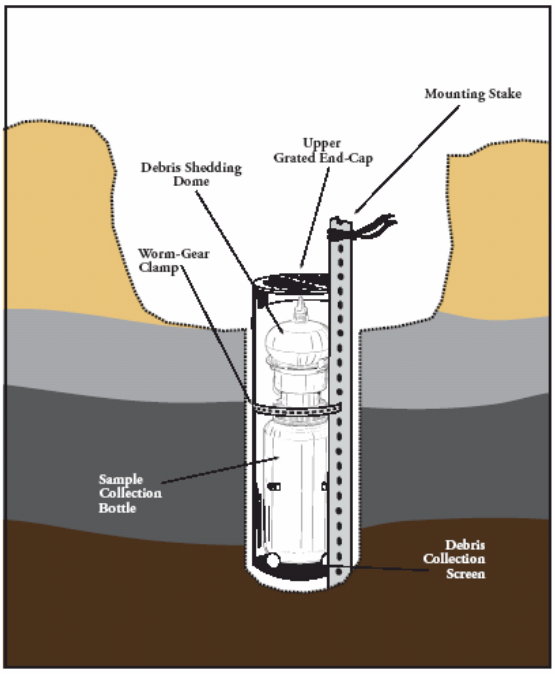
Table 4. Factors Affecting Dissolved Copper and Zinc Concentrations in Highway Runoff.

Factor	Dissolved Copper	Dissolved Zinc
Traffic Volume Factors		
ADT	X	X
Traffic Volume During Storm	X	
Traffic Volume during Antecedent Dry Period		X
Traffic Volume Preceding Storm		X
Precipitation Factors		
Antecedent Dry Period	X	X
Total Duration of Storm	X	X
Total Duration of Preceding Storm		X
Total Event Rainfall	X	X
Seasonal Cumulative Precipitation	X	X
Rainfall Intensity	X	X
Hydrologic Factors		
Volume of Flow per Unit Area of Watershed	X	X
Volume of Flow per Unit Area of Watershed During Preceding Storm		X
Environmental Factors		
Age of Pavement	X	X
Surrounding Land Use	X	X
Surrounding Vegetation	X	X
Watershed Area	X	X
Surrounding Soil Type	X	X
Soil Infiltration Rate	X	X

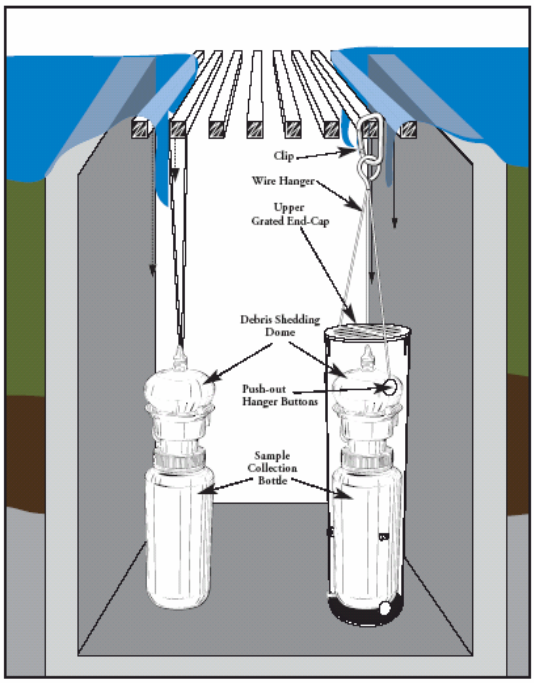
The plan would be to identify five AADT levels (e.g. 5,000; 10,000; 15,000; 20,000; and 25,000) for each of three precipitation regions (e.g. low, medium, and high rainfall areas). This would result in a total of 15 locations. Edge of Pavement and Outlet to Stream (or BMP inlet) samples would be taken at each location for a total of 30 samples per runoff event. To minimize costs, sampling could be performed using Nalgene sample bottles designed to capture the first liter of runoff from the site as shown in Figure 6.



Stream Mount



Ditch Mount



Grate Mount

Figure 6. Example of Nalgene Grab Sample Bottle Installations.

Information regarding land use, soil characteristics, and drainage areas would be obtained by combining aerial images and field reconnaissance surveys. Rainfall properties would be measured using on-site precipitation recorders. Ditch characteristics would be documented during installation of sample collectors. Pavement data would be obtained from WSDOT.

There are several important reasons for implementing this simplified approach. First, without preliminary data it is not possible to insure that any sampling strategy will be successful. Prior to embarking on a full-scale investigation, it is necessary to have sufficient Washington-based data to suggest the factors influencing metals concentrations are the same and that the spatial variations can be adequately determined. Second, decisions regarding the number of samples required can only be made once some estimate of mean concentrations and standard deviation can be made. Collecting this information would provide a basis for refining the sampling plan. And third, the costs associated with safely installing, operating, and maintaining automated samplers at a sufficient number of sites without assurances of success seem disproportionately high.

There are also several potential drawbacks to this approach. Samples would represent equilibrium concentrations rather than event concentrations because it would not likely be feasible to check all the sample locations every time it rained. These concentrations would be a result of sample holding times in excess of those recommended by and reported in Standard Methods. It may take several events to produce runoff at the Outlet to Stream locations. In addition, while the samples would reasonably represent the first liter of runoff, there would be no guarantee regarding the 1-hour maximum concentration. Finally, the time that Edge of Pavement samples are collected may not correspond with the Outlet to Stream samples due to delays in measurable runoff.

The implications of these simplifying assumptions need to be discussed and understood by all parties. However, the results would likely produce a multiple regression equation that would more accurately predict when metals treatment was required even if it did have relatively large error bars associated with the final results.

6.0 FINDINGS

The principal findings derived from this research and data evaluation include:

- There is no direct linear correlation between highway runoff pollutant event mean concentrations (EMCs) and AADT.

- Multiple linear regression analysis indicates that AADT, in conjunction with other factors, is related to the copper and zinc concentrations in California. These factors include but are not limited to antecedent dry period, duration of storm event, total event rainfall, seasonal cumulative precipitation, and adjacent land-use.

- In general, geographic region/characteristics appear to affect dissolved copper concentrations, but not dissolved zinc concentrations in California.

- Multiple linear regression models should only be applied in the geographic region and range of conditions represented by the original data set. Even then, the predictive capabilities of the model may not be acceptable.

- The data needed to populate such a regression model for the State of Washington do not currently exist.

- A considerable amount of information concerning peak hourly metals concentrations would need to be collected in order to be able identify cause and effect relationships for each of the contributing variables.

7.0 CONCLUSIONS

Based on analysis of the available literature it can be concluded that AADT is insufficient as a single predictor of both total and dissolved metal concentrations in highway runoff. Other factors that can have significant affects include but are not limited to antecedent dry period, geographical location, duration of storm event, total event rainfall, and seasonal cumulative precipitation. In addition, these factors have been reported to be interrelated, with no single factor being predictive. Currently there is insufficient data to develop a predictive equation that would be applicable to Washington State.

In accordance with Task 9 of this project, the findings of this study were presented to a Technical Advisory Committee (TAC) comprised of several representatives from both WSDOT and Ecology during a meeting held at WSDOT headquarters in October 2006. During this meeting, various aspects of the literature review, previous study conclusions, and data gaps were discussed. A particular concern emerged regarding the uncertainties demonstrated by the Caltrans data where the best predictive multiple linear regression equation based on EMC data demonstrated a R^2 of 0.508 for dissolved copper and a R^2 of 0.316 for dissolved zinc. It was also pointed out that this was for event mean concentration and that variability in peak hourly concentrations (as required by the WAC) would likely show even more unpredictability.

Consequently to develop a robust method of predicting metal concentration from highway runoff in Washington, a tremendous amount of additional data would have to be collected in all geographic regions of interest. It appears that geographical location (which affects precipitation patterns, intensity, duration, antecedent dry period, etc.) is a primary player in resulting metal concentrations. Therefore, subsequent efforts would need to focus on defining appropriate sample sites that would cover a range of conditions for Washington. Unfortunately, without hourly metals data to analyze, estimating the precise number of runoff and precipitation events required for statistical significance is not possible. However, based on TAC discussions concerning the various combinations of factors and the desired level of confidence to meet regulatory requirements, it was generally concluded that developing a sampling and analysis strategy resulting in a cost effective means of collecting the required data with sufficient quality assurances would not be feasible.

After discussing several possible avenues that could lead to improved criteria for assessing the need for enhanced metals treatment, the TAC began focusing on the question “When does

discharge need to be managed beyond basic treatment BMPs?" Contrasting points of view were raised regarding the issue of timing of highway stormwater discharges. On one hand it was argued that the worst pollutant loading would likely be after the long antecedent dry period that occurs during the summer. Combined with low stream discharges that typically occur during this period, a critical loading scenario could exist. On the other hand, it was suggested that much or all of this initial runoff would likely be infiltrated prior to reaching the stream thus making runoff from wet season winter storms the more critical condition. It was reiterated that Ecology's position would be that the edge of pavement would remain the compliance boundary barring hard, scientific evidence that could clearly show little to no runoff over a long-term simulation period.

This led to a fruitful discussion concerning the need for data and improved modeling tools to quantify water loss through infiltration from the edge of pavement to the stormwater outlet. To determine where infiltration is an effective treatment, more information would be needed concerning soil characteristics of highway shoulders, vegetated ditches, and infiltration losses from basic BMPs. Ecology was open to suggestions regarding diminutive flow situations as a result of infiltration and using this information to define areas of concern as well as areas that produce little or not runoff to surface water. However additional investigation was needed to insure adequate protection of water quality. Whether this means that Ecology would consider mixing zones near stormwater outfalls to larger streams is not clear. However, it appears that some method for quantifying the relative magnitudes of the stormwater load (flow * concentration) and stream load would be beneficial.

In western Washington, two simulation models currently exist that could potentially be modified to help with this investigation. Ecology's Western Washington Continuous Simulation Hydrology Model (WWHM) and WSDOT's MGS FLOOD could be modified and calibrated with infiltration data from highway stormwater conveyance systems throughout the state. However, since a continuous design model for eastern Washington does not currently exist, one would need to be developed. These models would need to be capable of simulating long-term hydrologic conditions (perhaps 100 years or more) to determine runoff rates for unlined conveyance systems under a variety of possible circumstances.

This information could be used to determine when and if the first plume of contaminants reach a stream. Combining this with information on fish utilization, background stream

concentrations, and other pertinent factors would enable quantification of ecosystem risk. This would mean collecting addition information regarding receiving water flow and concentration in relation to the timing of the first-flush plume reaching the stream.

When this information is available, a guidance document would need to be developed. This document would summarize the factors that would be indicative of situations where stormwater runoff would or would not be problematic. The guidance manual would include application of existing tools for different situations such as variable depths to groundwater, soil types, and precipitation rates. Subsequently, workshops explaining how to use the guidance manual would need to be conducted.

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APPENDIX A

WATER QUALITY CRITERIA FOR METALS

In natural streams and stormwater runoff, metals may be present in both dissolved and particulate forms. Since 1992, U.S. EPA has expressed criteria for these metals as dissolved rather than total. Dissolved metal is generally operationally defined as that metal which passes through a 0.45-micron (μm) filter. Consistent with U.S. EPA recommendations, Washington's WAC 173-201a promulgates surface water quality criteria for metals based on the dissolved fraction, and many of the criteria are expressed as a function of hardness (Table A1). Both acute and chronic metals criteria for cadmium, copper, lead, nickel, and zinc are expressed as functions of hardness.

As defined by the WAC and in Standard Methods, hardness is expressed as milligram (mg) equivalents of calcium carbonate ($CaCO_3$) per liter (L) and is calculated using the concentrations of calcium (mg/L) and magnesium (mg/L) according to the following equation:

$$\text{Hardness} = 2.497*Ca + 4.1189*Mg$$

As illustrated in Figure A1, as hardness increases, so does the allowable concentration of the metals. This occurs because the primary cationic components of hardness (calcium and magnesium) are non-toxic and can be readily absorbed by living organisms in direct competition with dissolved heavy metals. Therefore, as hardness increases, the bioavailability and, thus, toxicity of a given concentration of a particular metal decreases. Table A2 presents specific numeric criteria for acute dissolved copper and zinc. Because stormwater runoff occurrences are typically caused by short-term precipitation events, acute concentrations are characteristically used to measure impairment.

Table A1: Freshwater Dissolved Metals Criteria for Washington

Pollutant	Acute[1] (µg/L)	Chronic[2] (µg/L)
Cadmium	$\leq C_A\ (e^{(1.128\ [\ln(\text{hardness})]-3.828)})$	$\leq C_C\ (e^{(0.7852\ [\ln(\text{hardness})]-3.490)})$
	C_A is hardness dependent. At a hardness of 100, C_A is 0.944. For other hardness values: $C_A = 1.136672 - [(\ln \text{hardness})\ (0.041838)]$	C_C is hardness dependent. At a hardness of100, C_C is 0.909. For other hardness values: $C_C = 1.101672 - [(\ln \text{hardness})\ (0.041838)]$
Chromium (Hexavalent)	≤ 15.0	≤ 10.0
Chromium (Trivalent)	$\leq (0.316)e^{(0.8190\ [\ln(\text{hardness})] + 3.688)}$	$\leq (0.860)e^{(0.8190\ [\ln(\text{hardness})] + 1.561)}$
Copper	$\leq (0.960)(e^{(0.9422\ [\ln(\text{hardness})] - 1.464)})$	$\leq (0.960)(e^{(0.8545\ [\ln(\text{hardness})] - 1.465)})$
Lead	$\leq C_L\ (e^{(1.273\ [\ln(\text{hardness})] - 1.460)})$	$\leq C_M\ (e^{(1.273\ [\ln(\text{hardness})] - 4.705)})$
	C_L is hardness dependent. At a hardness of 100, C_L is 0.791. For other hardness values: $C_L = 1.46203 - [(\ln \text{hardness})\ (0.145712)]$	C_M is hardness dependent. At a hardness of 100, C_M is 0.791. For other hardness values: $C_M = 1.46203 - [(\ln \text{hardness})(0.145712)]$
Nickel	$\leq (0.998)(e^{(0.8460\ [\ln(\text{hardness})] + 3.3612)})$	$\leq (0.997)(e^{(0.8460\ [\ln(\text{hardness})] + 1.1645)})$
Zinc	$\leq (0.978)(e^{(0.8473\ [\ln(\text{hardness})] + 0.8604)})$	$\leq (0.986)(e^{(0.8473\ [\ln(\text{hardness})] + 0.7614)})$

Source: Washington Administrative Code, Section 173-201A-240
1 - A 1-hour average concentration not to be exceeded more than once every three years on the average.
2 - A 4-day average concentration not to be exceeded more than once every three years on the average.
The ambient criteria are for the dissolved fraction.

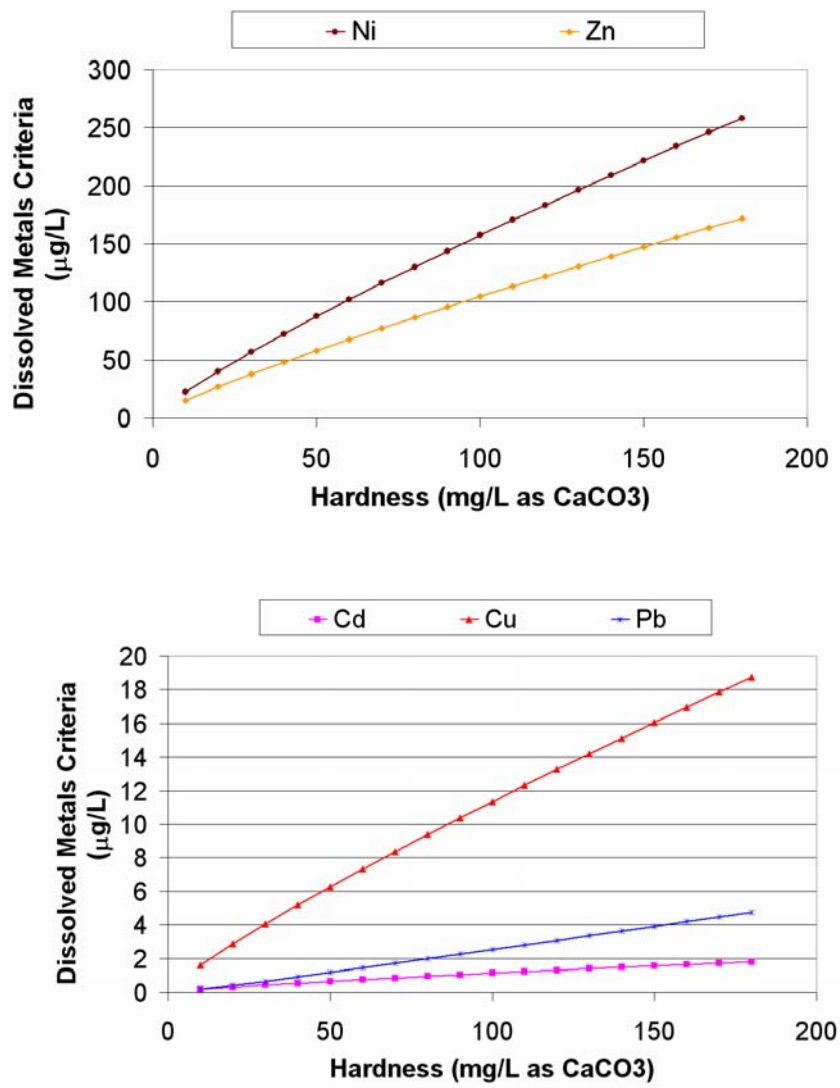

Figure A1. Washington State Metals Criteria as a Function of Hardness

Table A2. Summary of Hardness-dependent Acute Copper and Zinc Concentrations

Hardness	Acute Dissolved Copper (µg/L)	Acute Dissolved Zinc (µg/L)
10	1.9	16.3
15	2.8	22.9
20	3.7	29.3
25	4.6	35.4
30	5.5	41.3
40	7.2	52.7
50	8.9	63.6
60	10.5	74.2
70	12.2	84.6