Research Project Work Plan

for

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

SPR-663

Submitted by

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for

Oregon Department of Transportation
Research Unit
200 Hawthorne Ave. SE, Suite B-240
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1.0 Identification

1.1 Organizations Sponsoring Research

Oregon Department of Transportation (ODOT)
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1.3 Technical Advisory Committee (TAC) Members

Miguel Estrada, ODOT
Michele Eraut, FHWA
William Fletcher, ODOT, research proposer
Charlotte Kucera, ODOT
Matthew Mabey, ODOT, Chair

1.4 Friends of the Committee (if any)

Devon Simmons, NOAA
William VanPeeters, FHWA

1.5 Project Coordinator

Matthew Mabey, ODOT Research Unit

1.6 Project Champion

Frannie Brindal, ODOT Geo-Environmental

2.0 Problem Statement

Recent research has shown that very low concentrations of dissolved copper can inhibit the olfactory system of salmon listed as threatened and endangered (T&E) under the U.S. Endangered Species Act (ESA). Highway stormwater runoff is a source of copper to surface waters inhabited by T&E 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 T&E 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 (TDC) is partitioned between ionic and complexed forms in highway stormwater runoff and how that influences copper toxicity.

2.1 Background and Significance of Work

This study focuses on the concentration and speciation (*i.e.*, bioavailability) of copper, which is typically found in highway stormwater runoff, and has been shown to exhibit toxic effects on T&E fish species. At present, there is a gap in understanding between the known toxic effects of ionic copper and the concentrations of ionic copper present in highway stormwater runoff and natural receiving waters. Many studies have examined copper speciation in fresh and salt waters. In general, the majority of the total dissolved copper is complexed with organic matter and anions present in these waters, leaving extremely low concentrations of free ionic copper. Very few studies have investigated the speciation of copper in stormwater runoff, but it is anticipated that similar patterns exist.

By furthering the understanding of copper complexation with humic and fulvic substances from natural organic matter and other organic compounds that may be present in highway runoff (*e.g.*, compounds leached from tire rubber and unburned fuel residues), a more fundamental basis for evaluating the risk of copper in the environment (to ESA-listed salmon, in particular) will be realized. It is expected that governments and regulatory agencies across the country will use this information in Biological Assessments and Biological Opinions, and to define water quality criteria, regulations (*e.g.*, TMDLs and NPDES permits), and treatment requirements for copper-laden stormwater, reducing some of the current uncertainty in environmental impact assessment and project development.

The USDOT (2003) and USDOT-Research and Innovative Technology Administration (RITA) (2006) strategic plans list "Environmental Stewardship" as one of five strategic objectives. The desired outcomes under that objective are: 1) reduced pollution and other adverse environmental effects of transportation and transportation facilities and 2) streamlined environmental review of transportation infrastructure projects. The aims of this proposed research are indeed aligned with those outcomes.

3.0 Objectives of the Study

In planning, designing, and constructing or rehabilitating transportation facilities, ODOT is always balancing the State's transportation needs with environmental stewardship. Current assessments of the environmental impact of highway stormwater runoff are based on conservative estimates of copper toxicity. The trade-offs for these conservative assessments are lengthened project timelines and increased costs. In large part, the conservative estimate of copper toxicity (total dissolved copper) is used because little is known about copper speciation in stormwater. In other words, the fraction of the dissolved copper that is bioavailable and the extent to which that fraction interacts with other constituents (*e.g.*, calcium and magnesium) and biological organisms to exert toxicity is largely unknown. The proposed research aims to bridge that gap in understanding.

The objective of the proposed research is 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. Copper speciation and the concentrations of other constituents (*e.g.*, hardness and dissolved organic carbon) that influence copper toxicity are keys to this analysis and therefore are the focus of the proposed study. The overall objective of the research will be accomplished by answering the following questions:

(1) What are the concentrations and ratios of various copper species (*i.e.*, ionic, weakly complexed, and strongly complexed) in highway stormwater runoff and can those quantities be predicted (modeled) knowing something about key stormwater quality parameters?

(2) What are the concentrations of other water quality parameters that are known to influence copper toxicity (*e.g.*, hardness and dissolved organic carbon) in highway stormwater runoff?

(3) How do the metrics measured as part of (1) and (2) vary across the highway system, across seasons, and with impervious surface area, adjacent land use and traffic volume?

(4) Are there trends in commonly utilized measures of water quality (*e.g.*, total suspended solids, dissolved organic carbon) that can be correlated with copper speciation? If so, how do those parameters vary with the independent variables described in (3)?

(5) How do the concentrations and speciation of copper in highway stormwater runoff compare with the concentrations and speciation of copper in the surface receiving waters to which they are discharged and what are the potential impacts in terms of copper toxicity?

3.1 Benefits

Answering (1) will allow the estimation of the fraction of dissolved copper in stormwater that is likely to be bioavailable and successful development of an appropriate chemical equilibrium model will allow this prediction to be made knowing only basic water quality parameters. However, because speciation alone does not determine toxicity, the results from (2) are required to more fully assess the potential impact of a given stormwater. Questions (3) and (4) extend the analysis of (1) and (2), allowing ODOT to determine when, where, and why copper toxicity from highway runoff is likely to be the highest. Question (4) will give insight into what processes and constituents are responsible for complexing ionic copper; this insight will be useful in design of best management practices (BMPs) for stormwater treatment. The results from (5) will allow an analysis of the extent to which highway stormwater runoff is expected to impact the quality of the receiving waters in terms of copper toxicity.

Comparisons of the data from (1) and (2) and (5) with the current metric being used for Section 7 effects determinations (1 μg/L dissolved copper) will allow an evaluation of that guideline. The results of that evaluation will either justify the current methodology, or provide guidance for revising the metric to more appropriately account for copper bioavailability and toxicity. Regardless, this work will result in a more fundamental understanding of the impact of highway stormwater runoff with regard to copper toxicity; that understanding will be beneficial in the State of Oregon and across the country.

4.0 Background and Significance of Work

Highway stormwater runoff is a non-point source of many pollutants to surface receiving waters in the State of Oregon and across the United States. Because many of the pollutants found in stormwater are toxic, these discharges represent a potential threat to aquatic species. One contaminant of particular concern is copper. Copper is a common constituent in stormwater, with the primary sources being tailpipe emissions and the wear of tires, brake linings, moveable engine parts and asphalt pavement (Makepeace *et al.*, 1995). The toxicity of copper to a number of aquatic species ranging from diatoms, to fish has been shown (USEPA, 2007). For example, recent research by Sandahl *et al.* (2007) has shown that low concentrations (2-5 μg/L) of dissolved copper 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.

Taking these results into consideration, the National Marine Fisheries Service (NMFS) has changed the way it evaluates the potential impacts of transportation projects with regard to stormwater discharges to surface receiving waters inhabited by T&E species. Historically, Section 7 Biological Assessments were made by comparing pre- and post-project pollutant concentrations. Following the dissolved copper/salmon research, NMFS began basing effects determinations on dissolved copper concentrations as well. Consequently, even if an ODOT project decreases pre-project concentrations and loads of dissolved copper in runoff, if the concentration in post-project runoff is greater than 1 μg/L, NMFS may determine that project is “Likely to Adversely Affect” T&E species. As the severity of effects determinations increases, so does the potential for project delays and increased project costs (*e.g.*, requirements for advanced stormwater treatment).

In aquatic systems, copper partitions between the dissolved and particulate phases by adsorption processes. Additionally, in the aqueous phase, free (ionic) copper forms weak complexes with inorganic anions (*e.g.*, $Cu(OH)_2$) and strong complexes with dissolved organic matter. It is generally accepted that the ionic and weakly complexed fractions of the dissolved copper are the most bioavailable to aquatic species (Campbell, 1995; Paquin *et al.*, 2002). However, copper speciation is not the only factor that influences toxicity; as the concentration of hardness causing cations (calcium and magnesium) increase, copper toxicity decreases. This effect is conceptually framed as the competition between hardness cations and bioavailable copper for binding sites on the organism (Campbell, 1995; Paquin *et al.*, 2002). In light of these complicated interactions, it is clear that measurements of total, or even dissolved copper are conservative estimates of toxicity and do not result in a complete picture of the propensity of a given water to exert copper toxicity to aquatic organisms.

A number of researchers have investigated the speciation of copper in ambient freshwater and marine environments; recent examples include Bryan *et al.*(2002) and Ploger et al. (2005) (freshwater) and Buck and Bruland (2005), and Nuester and van den Berg (2005) (seawater). Results from these studies and previous research show that in natural waters, the vast majority of dissolved copper (90-99.9%) is strongly complexed with organic matter. However, despite the increased regulatory scrutiny surrounding copper, little is known about copper speciation in stormwater. In one study, Boulanger and Nioloaidis (2003) found that ionic copper concentrations ranged from <0.05 to 0.39 μg/L while the dissolved copper ranged from 8 to 14 μg/L in urban stormwater runoff from paved and grassy areas (much higher values were found in runoff from a copper roof and in the ambient receiving water). Here, the dissolved concentrations would raise a red flag when compared with the study by Sandahl *et al.*, but the concentrations of ionic copper (which is likely a better indicator of toxicity) were much lower. It is clear that an improved understanding of copper speciation in highway stormwater runoff is necessary to make fundamentally sound decisions regarding potential impacts.

A standardized test for the bioavailable fraction of dissolved copper does not exist. Furthermore, the recent EPA guidance document for determining copper criteria in ambient freshwater (USEPA, 2007), notes that such an approach is not justified due the heterogeneity of different surface waters and the fact that such a measure would not include the effects of hardness and pH. The EPA approved approach for determining the toxicity of a given freshwater is based on the use of a biotic ligand model (BLM) that accounts for copper speciation and binding to a biochemical site on an organism. Model inputs include temperature, pH, dissolved organic carbon, major geochemical cations (calcium, magnesium, sodium, and potassium), dissolved inorganic carbon (DIC, the sum of dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate), and other major geochemical anions (chloride, sulfate). To date, these methods give the greatest insight to copper toxicity and are the most broadly applicable. However, to our knowledge, these models have not been applied to stormwater systems, nor have the models been used to evaluate the potential toxicity to the olfactory system evidenced in recent research.

5.0 Implementation

The proposed work lies at the interface between several scientific disciplines (*e.g.*, civil engineering, environmental engineering, chemistry, biology, and toxicology) and different aspects of the proposed projects will be of interest to each group. Furthermore, there are a great number of stakeholders that are likely to be interested in the results; these include the general public, tribes, municipalities and State and Federal environmental and transportation agencies (*e.g.*, ODOT, Oregon DEQ, USEPA, USDOT, FWHA). As such, it anticipated that multiple outlets for technology transfer will be required to effectively disseminate the results to all interested parties.

Dissemination of the results to the scientific community will be accomplished through publication of the findings in appropriate peer-reviewed journals and oral or poster presentations at local and national conferences. Specific journals, trade journals and conferences will be selected in an attempt to reach a broad population of interested scientists and policymakers.

The results of the research will be directly communicated to the ODOT staff through workshops and targeted presentations. Results will also be directly communicated to NMFS biologists and researchers at OSU who performed many of the recent toxicological studies. It is hoped that the findings of this research will spur further research on the toxic effects of complexed copper and copper in stormwater matrices.

The environmental impacts of highway stormwater runoff are a current concern of DOTs around the country. Transportation officials from across the US will be reached through links to the research from relevant websites. For example, the American Association of State Highway and Transportation Officials (AASHTO) Center for Environmental Excellence (http://environment.transportation.org/), is a clearinghouse for environmental information for transportation professionals. The general public, local municipalities and Oregon transportation professionals will be reached through links to the research from the Oregon Department of Transportation’s Geo-Environmental Section webpage (http://www.oregon.gov/ODOT/HWY/GEOENVIRONMENTAL/index.shtml).

Finally, through the participation of graduate students, undergraduates, and K-12 students results will be further disseminated as those students continue their studies and begin careers in the public and private sector.

6.0 Research Tasks

Task	Responsible Party(ies)	Cost
Task #1: Literature Review The initial phase of the research will involve a thorough review of existing literature in the following areas: 1) concentration and speciation of copper in stormwater runoff and surface receiving waters in the State of Oregon and across the US; 2) evaluation of existing analytical techniques for measuring copper speciation in aqueous systems; and 3) identification of factors influencing the toxicity of copper to aquatic organisms. This literature review will give context to the problem and aid in the selection and/or development of appropriate analytical methods for copper speciation in stormwater. *Time Frame:* 9/2007-12/2008 *Deliverable:* Literature review text and accompanying citations. *TAC Decision/Action:* Approval or input regarding additional topics/information to be summarized.		$20,000

Task	Responsible Party(ies)	Cost
Task #2: Development of Field Sampling Plan A field sampling plan will be developed as a template for collecting highway stormwater runoff from sites around the state. The plan will aim to distribute sampling locations across up to eight (of the nine) level III ecoregions in the State (Thorson *et al.*, 2003). In up to three ecoregions (within a day trip of Corvallis), three separate sites with varying impervious area, adjacent land use, or traffic volume will be sampled. Final decisions regarding sampling locations (and which roadway characteristic to vary) will be made with guidance from ODOT and NMFS. The plan will include guidelines for sampling frequency, sample volume, and the number of samples to ensure the statistical validity of the results. In addition, procedures for collecting and preserving the samples will be presented. *Time Frame:* 9/2007-12/2008 *Deliverable:* Draft Sampling Plan *TAC Decision/Action:* Approval and/or input regarding additional sampling locations, frequency, or procedures.	OSU/TAC	$10,000

Task	Responsible Party(ies)	Cost
Task #3: Preliminary Sampling and Test/Select Analytical Methods Several analytical techniques have been used to determine copper speciation in water; these include voltammetry, ion selective electrodes, equilibrium dialysis, diffusive gradients in thin films, and extraction (*e.g.*, ion exchange, sorption, partitioning) followed by spectrometry. Based on the findings of the literature review completed as part of Task 1, preliminary laboratory studies using synthetic and natural waters and stormwaters will be performed to select and optimize the most appropriate method(s) for characterizing copper speciation in highway stormwater runoff. As part of this task, the sampling procedures outlined in Task 2 will be used to collect stormwater samples for use in the preliminary analysis. Analysis of these samples will be used to refine the analytical methods for copper speciation and other water quality parameters (*e.g.*, total suspended solids, alkalinity, dissolved organic carbon, hardness, ionic strength, major cations and anions). *Time Frame:* 11/2007-2/2008 *Deliverable:* Preliminary Data – Proposed Analytical Methods *TAC Decision/Action:* Approval and/or input regarding sampling procedures and proposed analytical methods.	OSU	$50,000

Task	Responsible Party(ies)	Cost
Task #4: Field Sampling and Laboratory Analysis Using the sampling plan developed as part of Task 2 and the analytical methods selected and refined as part of Task 3, a detailed field sampling program will be executed with the aim of characterizing copper speciation across the State as a function of season and roadway characteristics. Samples will be collected from one or more outfalls at each location using methods outlined in Task 2. Temperature and pH will be recorded in the field and the samples preserved and transported to the laboratory for further chemical analysis. Each sample will be analyzed for total copper, dissolved copper, and free (ionic) copper; the speciation of dissolved, complexed copper will also be analyzed. In addition to copper analysis, water samples will be analyzed for total suspended solids, alkalinity, dissolved organic carbon, hardness, conductivity, ionic strength, major cations (Na^+, K^+) and anions (Cl^-, SO_4^{2-}). If necessary, the makeup of the organic matter will be examined in further detail (*e.g.*, ratio of humic/fulvic acids). *Time Frame:* 3/2008-5/2009 (may extend longer if necessary) *Deliverable:* Data Summaries included in progress reports (see Task 7) *TAC Decision/Action:* Input regarding additional data collection, sampling procedures and data analysis.	OSU	$175,000

Task	Responsible Party(ies)	Cost
Task #5: Copper Speciation Modeling Using the total dissolved copper concentrations and water quality parameters measured as part of Task 4 as inputs, copper speciation will be modeled using established chemical equilibrium models (*e.g.*, MINEQL+, Visual Minteq, WHAM). Results from the modeling effort will be compared with the measured copper speciation. The primary objective of this task is to determine whether existing equilibrium models (particularly, the speciation component of the biotic ligand model) are capable of predicting copper speciation in highway stormwater runoff. If the speciation component of the biotic ligand model (BLM) is verified for stormwater, it will allow the effects of varying stormwater conditions on copper speciation to be simulated with a few basic parameters (*e.g.*, total dissolved copper, ionic strength, pH, alkalinity, and DOC). Any discrepancies between model predictions and experimental results will be used to revise the speciation model for stormwater systems. *Time Frame:* 7/2008-7/2009 *Deliverable:* Comparisons of modeling data and experimental data – to be included in quarterly progress reports (see Task 7). *TAC Decision/Action:* Input and evaluation	OSU	$30,000

Task	Responsible Party(ies)	Cost
Task #6: Copper Toxicity Modeling Upon validation in Task 5, copper speciation in stormwater will be linked with toxicity using the full biotic ligand model (BLM). Toxicity criteria for raw stormwater, ambient surface receiving waters, and mixtures of the two will be calculated (using EPA accepted LC_{50} values and the recent data on olfactory inhibition) and compared with the current NMFS guideline for assessing the impact of highway stormwater runoff. *Time Frame:* 1/2009-7/2009 *Deliverable:* Summary of Results in progress reports (see Task 7) *TAC Decision/Action:* Input and evaluation	OSU	$25,000

Task	Responsible Party(ies)	Cost
Task #7: Data Analysis/Final Report This task involves analyzing the data from the field sampling and analysis, copper speciation modeling, and toxicity modeling. Experimental measurements of copper speciation from the field sampling effort will be correlated with ecoregion, season, roadway characteristics and water quality parameters to identify which variables have the greatest influence and have the potential to be used as a indicator for copper toxicity. Comparisons of the field sampling data with equilibrium and toxicity models will be used to further define the important parameters determining copper speciation and the extent to which highway stormwater runoff is expected to pose a toxic threat to aquatic species, particularly ESA-Listed fish species. *Time Frame:* 11/2007-9/2009 *Deliverable:* Final Report (progress reports to be submitted approximately every 3-4 months). Peer-reviewed journal articles and conference presentations will also be prepared from the data/results of the study. *TAC Decision/Action:* Approval	OSU	$75,000

The literature review, sampling plan and progress reports will be submitted as written documents, or communicated directly to the TAC through oral/multi-media presentations. The final report will be produced in the standard ODOT Research Group report format unless some other format is deemed to be more appropriate as a supplement to the ODOT format.

7.0 Time Schedule

The proposed work plan has been divided into 7 tasks spanning 25 months. The schedule of project tasks is shown below.

Project Tasks	FY 08												FY 09												FY 10		
	Qtr 1			Qtr 2			Qtr 3			Qtr 4			Qtr 1			Qtr 2			Qtr 3			Qtr 4			Qtr 1		
	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Task 1: Literature Review Deliverable: Literature Review						*																					
Task 2: Preliminary Sampling Plan Deliverable: Sampling Plan						*																					
Task 3: Preliminary Sampling & Test/Select Analytical Methods Deliverable: Preliminary Data								*																			
Task 4: Field Sampling & Laboratory Analysis Deliverable: Progress Report												+				+				+							
Task 5: Speciation Modeling Deliverable: Progress Report																+				+				+			
Task 6: Toxicity Modeling Deliverable: Progress Report																								+			
Task 7: Data Analysis & Final Report Deliverable: Final Report												*				*				*				*			*

* Deliverables

+ Data feeds to progress reports submitted as intermediate deliverables under Task 7

8.0 Budget Estimate

An itemized budget for the project is included here, showing expenditures for each item by fiscal year and in total.

	FY08	FY09	FY10	Total
Personnel				
J. Nason	$0	$9,872	$12,202	$22,074
P. Nelson	$0	$9,000	$9,000	$18,000
M. Azizian	$8,756	$9,020	$0	$17,776
Graduate Assistant 1	$16,170	$21,560	$5,390	$43,120
Graduate Assistant 2	$16,170	$21,560	$5,390	$43,120
Undergraduate 1	$3,250	$3,250	$0	$6,500
Undergraduate 2	$0	$3,250	$3,250	$6,500
Total Salaries	**$44,346**	**$77,512**	**$35,232**	**$157,090**
Fringe Benefits				
J. Nason	$0	$2,468	$3,050	$5,518
P. Nelson	$0	$2,250	$2,250	$4,500
M. Azizian	$2,320	$2,390	$0	$4,710
Graduate Assistant 1	$1,455	$2,102	$539	$4,096
Graduate Assistant 2	$1,455	$2,102	$539	$4,096
Undergraduate 1	$37	$37	$0	$74
Undergraduate 2	$0	$37	$37	$74
Total Fringe Benefits	**$5,267**	**$11,386**	**$6,415**	**$23,068**
Tuition				
Graduate Assistant 1	$9,123	$11,102	$1,757	$21,982
Graduate Assistant 2	$9,123	$11,102	$1,757	$21,982
Total Tuition	**$18,246**	**$22,204**	**$3,514**	**$43,964**
Total Personnel Costs	**$67,859**	**$111,102**	**$45,161**	**$224,122**
Travel	**$9,500**	**$9,000**	**$3,500**	**$22,000**
Services and Supplies	**$21,296**	**$13,696**	**$5,000**	**$39,992**
Total Direct Costs	**$98,655**	**$133,798**	**$53,661**	**$286,114**
Total Indirect Costs	**$33,900**	**$47,048**	**$21,142**	**$102,090**
Total Project Costs	**$132,555**	**$180,846**	**$74,803**	**$388,204**

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