Copper Water-Effect Ratio Study for Discharged Effluent to Humboldt Bay from Elk River Wastewater Treatment Plant, City of Eureka.

Prepared for:

Michael Hansen
Water Quality Supervisor
City of Eureka
4301 Hilfiker Lane
Eureka, CA 95503

Prepared by:

Matthew Hurst, Ph.D.
Department of Chemistry
Humboldt State University
Arcata, CA 95521

February 28, 2016

Acronyms and Abbreviations

BOD	Biological Oxygen Demand
CCC	Criterion Continuous Concentration
CMC	Criterion Maximum Concentration
CTR	California Toxic Rule
CWA	Clean Water Act
EC_{50}	50% or Median Effect Concentration
ELAP	Environmental Laboratory Accreditation Program
EPA	Environmental Protection Agency
fWER	Final Water Effect Ratio
L	Liters
mgd	Million Gallons per Day
mg/L	Milligrams per Liter
µg/L	Micrograms per Liter
NPDES	National Pollution Discharge Elimination System
ppt	Parts per Thousand
SIP	Statewide Implementation Plan
SMAV	Species Mean Acute Value
SSO	Site Specific Objective
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
WER	Water Effect Ratio
WWTF	Wastewater Treatment Facility
WQBEL	Water Quality Based Effluent Limitation

Table of Contents

1. INTRODUCTION

1.1 Background

The City of Eureka is seeking a renewal of the National Pollution Discharge Elimination System (NPDES) permit from the Regional Water Board, which sets water quality-based effluent limitations for several constituents, including copper. Under the previous NPDES permit (expired July 24, 2014), wastewater plant effluent discharged to Humboldt Bay (Discharge Point 001) from Elk River WWTF must contain less than 33 ppb (six-month median) and 312 ppb (maximum daily) of total recoverable copper.[1] The study has investigated whether these effluent limitations at Discharge Point 001 are appropriate given the chemical composition of the discharged effluent and receiving waters. Copper toxicity tests were performed on undiluted plant effluent and the receiving waters of Humboldt Bay to determine the median effect concentration (EC_{50}), which is a standard measure of copper toxicity to sensitive organisms. Because Discharge Point 001 is currently classified as an ocean discharge, these toxicity tests used larvae of *Mytilus galloprovincialis* (*M. galloprovincialis*, Mediterranean mussel) as the test organism. *M. galloprovincialis* is found along the coast of California and is closely related to the native *Mytilus edulis*, or common mussel. The *Mytilus sp.* is commercially important along the California coast and is listed as the most sensitive species used for measuring copper toxicity in saltwater.[2] The test results using *Mytilus galloprovincialis* allow for the calculation of a site-specific water-effect ratio (WER) for copper at Discharge Point 001. This final report summarizes the work performed in the study and recommends new effluent limitations for copper at the Elk River Wastewater Treatment Plant to the Regional Water Quality Control Board.

Copper in natural waters is capable of causing a toxic response in sensitive aquatic species.[3] To better understand the role of copper and its toxic effect on biology, one must be able to determine the various chemical forms or species of copper and their respective concentrations. In the case of copper, toxicity to sensitive aquatic species like *Mytilus sp.* has been demonstrated to be a function of the hydrated free cupric ion species concentration ($Cu^{2+}_{(aq)}$), rather than the total recoverable or dissolved copper concentration.[4] Although copper is toxic at low levels, it is also a micronutrient required by biology. This "not too little" and "not too much" reality for copper has been framed as the "Goldilocks" condition.[5] For this reason, it is important to determine the amount of bioavailable (i.e., toxic) copper that exceeds the amount required by the most sensitive species in an aquatic system.

1.2 The Water-Effect Ratio

The bioassay method used to calculate the WER determines the EC_{50} for a sensitive aquatic species in the presence of elevated copper concentrations using toxicity tests on site-specific water and laboratory water. The WER is calculated by taking the EC_{50} of site water and dividing by the EC_{50} of laboratory water (Eqn 1),

$$WER = \frac{SiteWaterEC_{50}}{LabWaterEC_{50}}. \quad \text{(Eqn 1)}$$

The EC_{50} of laboratory water is substituted by the species mean acute value (SMAV) in the calculation if the EC_{50} of laboratory water is smaller than the SMAV.[6] This results in a more conservative value for the WER. The SMAV for *Mytilus sp.* and the dissolved copper fraction is 6.19 mg/L.[2] If the site-specific water is less toxic than the laboratory water, the WER value for the site-specific water will be greater than 1.0. Alternatively, if the water chemistry within the site-specific water exhibits more acute toxicity relative to laboratory water, then the WER value will be less than 1.0.

1.3 Participants in the WER for Copper Study

A summary of participating personnel and their role in the WER for copper study is as follows:

- *City of Eureka (Michael Hansen, Water Quality Supervisor)*: Responsible for coordinating sample transport, managing chain of custody and laboratory results, ordering laboratory tests, assisting in sampling, measuring temperature and pH at the time of sample collection, and calculating effluent flow. The City of Eureka is an ELAP certified laboratory and will analyze for TSS and BOD in effluent samples as described in *Streamlined Water-Effect Ratio Procedure of Discharges of Copper*.[6]

- *WER Consultant (Matthew Hurst, Ph.D.)*: Responsible for collecting samples using trace-metal clean techniques and collecting visual observations during sampling. Other responsibilities included writing the Study Plan, data analysis, and WER final report preparation.

- *Bioassay Laboratory (Pacific EcoRisk)*: Responsible for supplying acid-cleaned containers for transporting bioassay samples, performing the copper toxicity tests on undiluted effluent samples and Humboldt Bay samples using *M. galloprovincialis* as the test organism. Other responsibilities included coordinating sample testing in-house or at a certified analytical laboratory, sending out samples for copper testing, data and statistical analysis, and generating a laboratory report containing WER results.

- *Analytical Laboratory (Caltest)*: Responsible for chemical analyses necessary for the WER report as listed in the *Streamlined Water-Effect Ratio Procedure of Discharges of Copper*.[6] These chemical analyses were subcontracted out by Pacific EcoRisk as needed. Caltest was responsible for performing the copper analyses pertaining to the toxicity testing.

1.4 Study Purpose

The purpose of this study is to determine the site-specific WER for total recoverable copper at Discharge Point 001 at the Elk River WWTP using EPA-approved methodology. Copper toxicity testing on undiluted effluent samples and the receiving waters of Humboldt Bay using *M. galloprovincialis* as the test organism was carried out over two sampling events more than one month apart. The resulting site-specific WER provides the necessary scientific data to determine the appropriate discharge limit for copper at the outfall and replace the "rebuttable" WER default value of 1.0.[7] The study was guided by the *Streamlined Water-Effect Ratio Procedure of Discharges of Copper*.[6] The study also used the *California Toxics Rule* (CTR)[7], *Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California* (Statewide Implementation Plan or SIP)[8], and the *California Ocean Plan*[9] to provide guidance in determining the best protocols for the specific site.

Although Elk River WWTP receives a 30:1 dilution credit for copper at Discharge Point 001, it was recommended by the Water Board that a WER for copper be determined for the undiluted effluent (Michael Hansen, personal communication). These WER results will show that the ambient copper in the effluent is not bioavailable and that there exists excess dissolved organic matter in the effluent that provides further buffering capacity with increased copper. A WER for the receiving waters of Humboldt Bay was also determined in order to show the potential effects of discharging effluent containing copper to the marine system. The WER for the receiving waters will be used to reevaluate the default WER value of 1.0 and determine a new site-specific objective (SSO).[7] The comparison of copper toxicity between the undiluted effluent and receiving waters allows for a more comprehensive study and understanding of the ocean discharge. This conservative approach in calculating the final WER values and new effluent limitations at Discharge Point 001 ensures that sensitive aquatic species in receiving waters are protected.

2. Methods

2.1 Sample Site and Conditions

Elk River WWTF is situated on the east side of Humboldt Bay near the mouth of the Elk River (Figure 1). The plant has an average dry weather design treatment capacity of 5.24 mgd and uses primary clarifiers, trickling filters and secondary clarifiers to treat the wastewater for approximately 45,000 residents in the greater City of Eureka area. The secondary effluent is temporarily stored in a holding basin prior to being dechlorinated and discharged to the receiving waters of Humboldt Bay at the beginning of the ebb tide.

Humboldt Bay is highly influenced by the coastal ocean with a tidal prism of 7.4×10^7 m^3 (2.0×10^{10} gallons) and has minimal freshwater input.[10] The Discharge Point 001 is located on the east side of the shipping lane in Humboldt Bay near the bay entrance and is equipped with an end-of-pipe diffuser that delivers a 30:1 dilution of the effluent prior to discharging to the receiving waters. The sample site for the collection of the receiving waters was accessed by boat and was near the location of the end-of-pipe diffuser (Figure 1).

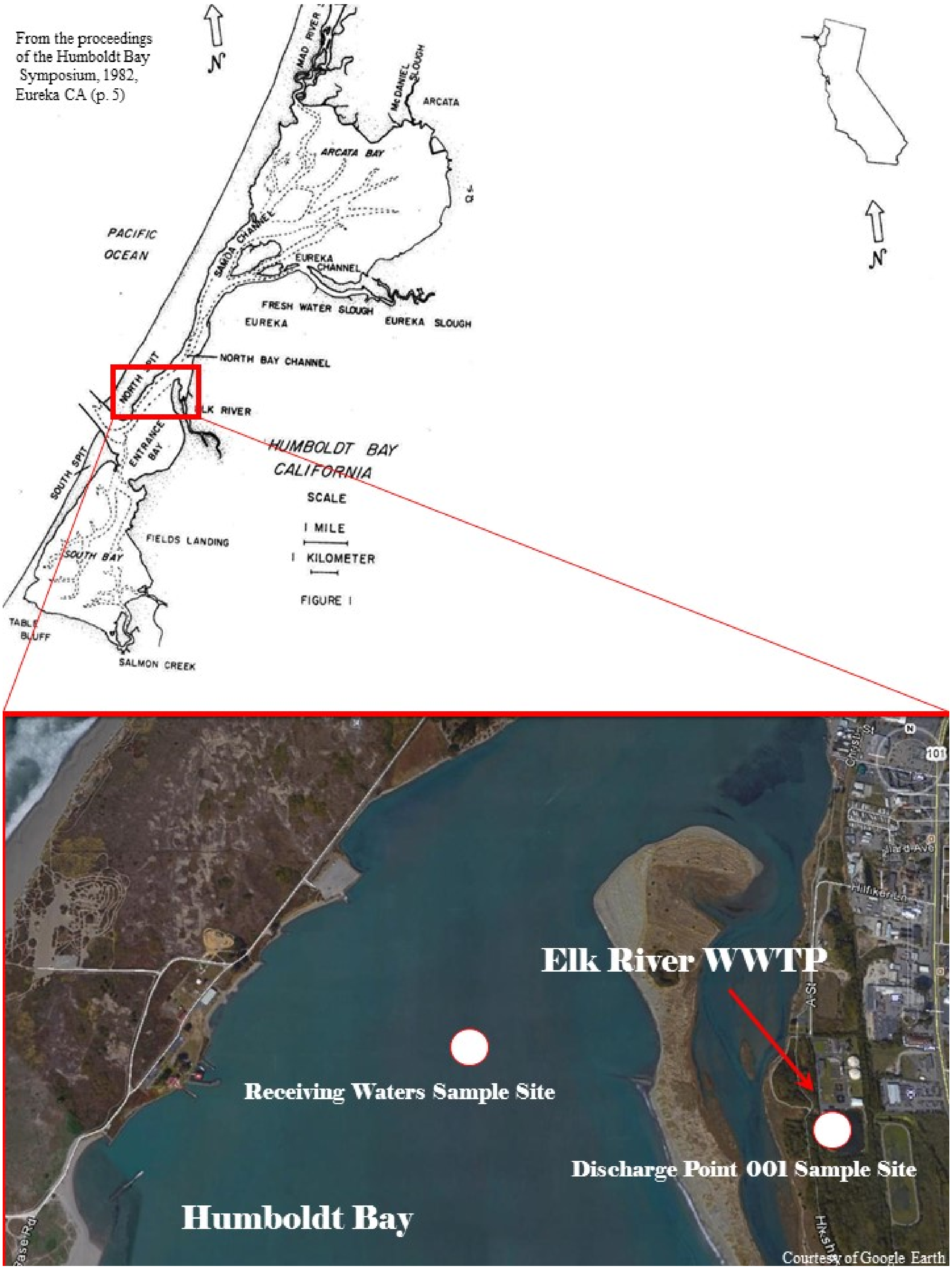

Figure 1: Site Map of Elk River WWTF and main channel of Humboldt Bay with sampling locations.

Weather conditions preceding the two sampling events were conducive to average or better operating conditions at Elk River WWTF for this seasonal period. The months of September, October and the beginning of November had below-average rainfall and warmer than average temperatures. For Event 1 (10/6/15), the maximum temperature matched the current monthly average of 65˚F, and negligible precipitation fell in the three weeks prior to sample collection. For Event 2 (11/10/15), the maximum temperature was 1˚F above the maximum average and measurable precipitation fell in the three weeks prior to sampling. The National Weather Service office at Woodley Island in Humboldt Bay reported that 0.49 inches of rainfall were recorded on November 8-9 and previous to that 0.67 inches of rainfall were recorded on November 1-2. Overall, 2.0 inches of precipitation occurred in the three weeks prior to the sampling of Event 2.

The Elk River WWTF was operating at average to better conditions, as measured by BOD, TSS and turbidity, for the October-November period (Table 1 and 2). The two sampling events over one month apart were performed before the beginning of the wet season. The daily flow of 3.69 mgd for Event 1 was below the average daily flow for the month of October 2015 (Table 2). The flow of 4.67 mgd on the day of Event 2 was 15% above the monthly average and was due to the 0.49 inches of rainfall that occurred over the two days prior to the sample collection. All of the water quality parameters of the effluent samples for Events 1 and 2 were within the monthly ranges for pH, turbidity, TSS and BOD (Table 1 and 2). For the effluent sample, the TSS was below monthly averages during each event and the temperature during Event 2 was considerably lower than Event 1, which was due to lower night-time temperatures. For the receiving waters of Humboldt Bay, the turbidity was low and the salinity was constant at 34 ppt for both sampling events, suggesting that there was no influence from freshwater runoff during Event 2 (Appendix 1, pg 2 in Laboratory Report, Table 2).

Water Quality Parameters and Daily Flow	**Site and Date of Collection**			
	Discharge Point 001		**Receiving Waters (Humboldt Bay)**	
	Event 1 (10/6/15)	**Event 2 (11/10/15)**	**Event 1 (10/6/15)**	**Event 2 (11/10/15)**
Temperature (C °)	20.4	16.8	10.6	12.6
pH	6.6	6.8	7.9	7.9
Turbidity (NTU)	4.6	6.2	3.2	3.5
TSS (mg/L)	5.6	6.8	-	-
BOD (mg/L)	11	5.8	-	-
Daily Flow (mgd)	3.69	4.67	-	-

Table 1: Ambient conditions and parameters showing plant performance at the time of sample collection.

Water Quality Parameters and Daily Flow	Monthly Averages and Ranges (min.-max.)					
	July	**August**	**September**	**October**	**November**	**December**
pH	7.0 (6.6-7.1)	6.9 (6.8-7.1)	6.7 (6.1-6.9)	6.6 (6.4-6.9)	6.6 (6.4-6.8)	6.5 (6.1-6.8)
Turbidity (NTU)	7.8 (5.6-13)	8.0 (5.8-12)	5.6 (4.1-7.9)	5.7 (4.3-9.3)	6.8 (5.5-8.1)	8.0 (6.0-15)
TSS (mg/L)	18 (14-21)	20 (16-26)	12 (10-15)	8.8 (5.0-12)	8.3 (7.6-9.2)	10 (7.6-13)
BOD (mg/L)	19 (16-22)	21 (14-24)	15 (13-18)	9.1 (6.3-13)	9.3 (5.8-11)	10 (6.4-14)
Daily Flow (mgd)	3.90 (3.4-4.4)	3.73 (3.3-4.3)	3.62 (3.3-4.2)	3.59 (3.3-4.0)	4.05 (3.2-5.7)	8.54 (3.9-17.7)

Table 2: Average and range values for water quality parameters from July-December of 2015.

2.2 Sample Collection and Handling

Grab samples were collected at the designated NPDES monitoring station at Elk River WWTP for Discharge Point 001 and by boat in the main channel of Humboldt Bay near the end-of-pipe discharge point. Samples of the effluent and receiving waters were collected on September 28, 2015 for use in range-finding tests. The sampling for Event 1 and 2 was performed on October 6 and November 10, respectively. All sampling was conducted by WER consultant Matthew Hurst and City of Eureka Water Quality Supervisor Michael Hansen using EPA methods and trace metal-clean techniques.[11-13] The effluent samples were collected during the routine discharge of effluent to Humboldt Bay at the beginning of ebb tide. The effluent is pumped from the holding basin and the pressurized sample was collected from a spigot at the NPDES monitoring station. The receiving waters sample was collected by boat using a peristaltic pump and extension pole, equipped with acid-cleaned Teflon and C-flex tubing.[12] This sample was collected 30-60 minutes prior to the effluent discharge and at a depth of 8 ft. The samples were stored in acid-cleaned, 10-L high-density polypropylene carboy provided by Pacific EcoRisk. Each container was rinsed three to four times with sample prior to filling with sample. Temperature measurements were taken for each sample at the time of collection (Table 1).

The individual carboys were transferred to the water quality laboratory at Elk River WWTF, where under chain of custody, sample containers were kept in ice chests at < 4˚C. The effluent and receiving water samples were shipped overnight in separate ice chests under conditions of < 4˚C to Pacific EcoRisk. Handling of the samples after the arrival to Pacific EcoRisk is described in *Performance of Mytilus galloprovincialis Toxicity Testing in Support of Development of a Copper Water-Effect Ratio for Application to the City of Eureka Elk River Wastewater Treatment Plant* Report (Appendix 1, pp. 1-2 in Laboratory Report). The chain of custody reports for the collection and delivery of these samples to Pacific EcoRisk for Event 1 and 2 can be found in Appendix A of the Laboratory Report.

2.3 Laboratory Procedures

Pacific EcoRisk followed laboratory procedures as described in the *Streamlined Water-Effect Ratio Procedure of Discharges of Copper* and the *Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms*.[6,14] The undiluted effluent and Humboldt Bay water samples were tested for copper toxicity and for chemical parameters necessary for interpreting results.[6] Since the Elk River WWTF effluent is discharged to a marine environment, *Mytilus galloprovincialis* was used as the test specimen. Upon selecting *Mytilus galloprovincialis*, the undiluted effluent sample was salted to a salinity of 30 ppt prior to the toxicity test. A range-finding test was conducted starting September 29, 2015 and provided information on the appropriate copper additions to be used during the definitive tests.

Total recoverable copper was measured using ICP-MS methodology to a maximum reporting limit of 2.5 μg/L and a detection limit of 0.75 μg/L. The copper source used to spike samples was copper (II) chloride (ACS reagent grade, VWR) (Appendix 1, pg. 2 in Laboratory Report).

The laboratory water was 1 µm-filtered seawater from U.C Granite Canyon Marine Laboratory (Carmel, CA) diluted to 30 ppt for comparison with the salted effluent sample. It was necessary to perform a second laboratory water test due to the high salinity in the receiving waters. This second laboratory water consisted of undiluted, 1 µm-filtered seawater and the toxicity results were compared to the receiving waters; both test solutions had a salinity of 34 ppt (Appendix 1, pg. 2 in Laboratory Report).

The 48-hour toxicity tests on laboratory water, Discharge Point 001 and the receiving waters of Humboldt Bay using *Mytilus galloprovincialis* as the test organism were initiated on October 7 (Event 1) and November 12 (Event 2) by Pacific EcoRisk. Temperature, dissolved oxygen and pH were monitored throughout the toxicity tests. Details of experimental design, acclimation and toxicity test procedures, testing parameters, reference toxicant testing, statistical methods and data analysis by Pacific EcoRisk can be found in the *Performance of Mytilus galloprovincialis Toxicity Testing in Support of Development of a Copper Water-Effect Ratio for Application to the City of Eureka Elk River Wastewater Treatment Plant* Report (Appendix 1, pp. 1-5 in Laboratory Report).

BOD and TSS analyses were conducted by the ELAP certified laboratory at Elk River WWTP. These tests were performed to show that the plant was working at normal or above normal conditions.

2.4 Quality Assurance and Quality Control (QA and QC)

U.S. EPA methods were followed throughout the course of sampling and during the performance of toxicity testing.[6,11,14] The analytical laboratory results showed that laboratory control samples (LCS), laboratory control sample duplicates (LCSD) and blanks were within acceptable range. Details of the quality assurance and quality control data from the analytical laboratories can be found in *Performance of Mytilus galloprovincialis Toxicity Testing in Support of Development of a Copper Water-Effect Ratio for Application to the City of Eureka Elk River Wastewater Treatment Plant* Report (Appendix 1, pp. 13-18 in Laboratory Report).

All conditions of conducting a WER study for copper were met with two exceptions.

1. Upon delivery to the Pacific EcoRisk laboratory, the receiving water sample collected on October 6, 2015 arrived with a temperature exceeding 6 ˚C with a value of 6.9 ˚C (Appendix 1, pg. 11). The receiving water sample was packaged exactly the same as the effluent sample for Event 1. The effluent sample arrived to Pacific EcoRisk at a temperature 1.9 ˚C even though its ambient temperature was greater (Table 1). The temperature values of all samples upon arrival to Pacific EcoRisk are summarized in Appendix 1, pg. 2 in Laboratory Report, Table 2.

In Section 8 of the *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*,[14] the methods specific to effluent sample handling are addressed. In particular, Section 8.5.1 states:

"Unless the samples are used in an on-site toxicity test the day of collection (or hand delivered to the testing laboratory for use on the day of collection), it is recommended that they be held at 0-6°C until used to inhibit microbial degradation, chemical transformations, and loss of highly volatile toxic substances."

Although it is "recommended" the samples be held at 0-6°C, it is not "required" or that they "must" be kept in the 0-6°C temperature range. Also, the purpose is to "inhibit microbial degradation, chemical transformations, and loss of highly volatile toxic substances." Considering the overnight delivery of the sample packed in ice and the initiation of the copper toxicity test the day after sampling, these concerns are not an issue.

2. The total suspend solids (TSS) analyses for samples and laboratory water in Event 1 were performed after the holding time. The effluent, receiving water and laboratory (30 ppt and 34 ppt) were initially analyzed for TSS but the dissolved solids were not rinsed prior to drying and weighing the sample. This resulted in high values. The analysis is addressed by Pacific EcoRisk and Caltest Analytical Laboratory in Appendix 1, pg. 13 in Laboratory Report and Appendix D therein.

3. Results

3.1 Water Quality of Effluent and Receiving Waters

The water quality parameters taken upon arrival to Pacific EcoRisk are summarized in Table 3 and are also included in the *Performance of Mytilus galloprovincialis Toxicity Testing in Support of Development of a Copper Water-Effect Ratio for Application to the City of Eureka Elk River Wastewater Treatment Plant* (Appendix 1, pg. 2 in Laboratory Report). These results show relatively consistent water quality conditions between the two sampling events for each sample.

Water Chemistry Parameters	**Discharge Point 001**		**Humboldt Bay (receiving waters)**	
	Event 1 (10/6/15)	Event 2 (11/10/15)	Event 1 (10/6/15)	Event 2 (11/10/15)
D.O. (mg/L)				
pH	7.07	6.79	7.68	7.84
Conductivity (µS/cm)	1143	864	52,300	52,500
Salinity (ppt)	0.6	0.5	34.2	34.0
Temperature (˚C)	1.9	0.7	6.9	0.4
Ammonia (mg/L N)	4.04	4.38	< 1.0	< 1.0
TSS (mg/L)	5	10	4	6
DOC (mg/L)	11.7	12.0	0.836	0.926
Dissolved Copper (µg/L)	22.9	24.3	< 2.5	< 2.5

Table 3: A summary of water chemistry parameters in site-specific waters. Note: TSS values for Event 1 samples were reanalyzed beyond the holding time. The TSS for the effluent, prior to being salted, was also analyzed by the City of Eureka within the holding time (Table2).

3.2 Copper Toxicity to Mytilus galloprovincialis

Copper toxicity tests using *Mytilus galloprovincialis* were initiated with range-finding tests on September 28. A summary of the results for the range-finding test on effluent and receiving waters samples can be found in Appendix 1, pg. 3 in Laboratory Report. The definitive toxicity testing for Events 1 and 2 was initiated on October 7 and November 12, 2015, respectively. The results using nominal test concentrations for the effluent and receiving waters can be found in Appendix 1, pp. 6-10 in Laboratory Report. During the 48-hour definitive toxicity testing the dissolved oxygen and temperature were monitored at the beginning and end of the test. Temperature was monitored each day of the definitive toxicity test. The water quality parameters were in acceptable range, and the variations of temperature and dissolved oxygen can be found in the Appendix 1, pp. 12-13 in Laboratory Report.

3.3 Calculation of the Water Effect Ratio for Copper

The 48-hour toxicity tests determined the EC_{50} for *Mytilus galloprovincialis* in samples and laboratory waters. The EC_{50} results for laboratory water and site-specific water were compared to both the effluent and receiving water samples and were used in copper WER calculations.

Since the laboratory water and samples were adjusted to have the same seawater matrix, normalization of the EC_{50} values based upon hardness was not necessary. Prior to calculating the WER for each event, the EC_{50} for the laboratory water was compared to the species mean acute value (SMAV) for *Mytilus sp.*. The larger value is used in the calculation of the WER. The SMAV for *Mytilus sp.* for the dissolved copper fraction is 6.19 mg/L.

Using Eqn. 1, the WER for the site-specific water was calculated by dividing the site-specific water EC_{50} by the laboratory water EC_{50} or SMAV, whichever value is larger. This calculation was performed on each undiluted effluent sample (salinity adjusted to 30 ppt) and Humboldt Bay water sample (salinity of 34 ppt) taken during the two sampling events over one month apart. The effluent sample was compared to the standard laboratory water adjusted to a salinity of 30 ppt, while the Humboldt Bay water sample was compared to the laboratory water with a salinity of 34 ppt.

The geometric mean of the two WER values produce the Final WER (fWER) for each sample (Eqn 2). The geometric mean is determined by multiplying the two site-specific WER values together and then taking the square root of that value.

$$Final\ WER = (\ WER_1 + WER_2)^{1/2} \qquad \text{(Eqn 2)}$$

The definitive copper toxicity test results are summarized in Table 4 and 5. The EC_{50} values for effluent samples, receiving waters and laboratory water (30 ppt and 34 ppt) are listed along with the calculated WER for the total recoverable copper fraction. In both Event 1 and 2, the EC_{50} of the laboratory water was greater than SMAV and therefore the EC_{50} was used in the calculation of the WER.

WER – Event 1	**Test Waters**	
	Effluent	**Receiving Waters**
Sample EC_{50} (μg/L)	159	14.0
Laboratory Water EC_{50} (μg/L)	11.7 [a]	11.8 [b]
SMAV (μg/L)	6.19	6.19
WER	**13.6**	**1.2**

Table 4: A summary of EC_{50} values in test waters for WER – Event 1. All values are with respect to the recoverable copper fraction. EC_{50} values were determined in laboratory water with a salinity of *a)* 30 ppt and *b)* 34 ppt.

WER – Event 2	**Test Waters**	
	Effluent	**Receiving Waters**
Sample EC_{50} (μg/L)	138	13.1
Laboratory Water EC_{50} (μg/L)	11.8 [a]	9.39 [b]
SMAV (μg/L)	6.19	6.19
WER	**11.7**	**1.4**

Table 5: A summary of EC_{50} values in test waters for WER – Event 2. All values are with respect to the recoverable copper fraction. EC_{50} values were determined in laboratory water with a salinity of *a)* 30 ppt and *b)* 34 ppt.

The WER values for each event are summarized in Table 6. The fWER value for the undiluted effluent at Discharge Point 001 was 12.6, and the fWER for the receiving waters of Humboldt Bay was 1.3.

Sampling Event	**Sample Site**	
	Discharge Point 001 Effluent	**Humboldt Bay Receiving Waters**
WER – Event 1 (10/6/15)	13.6	1.2
WER – Event 2 (11/10/15)	11.7	1.4
Final WER (total recoverable copper)	**12.6**	**1.3**

Table 6: Calculation of Final WER values for each effluent and receiving waters sample. Final WERs are the geometric means of the two values and are with respect to the total recoverable copper fraction.

3.4 Recommended Water Effect Ratio and Site Specific Objective for Copper

The fWER values for the undiluted effluent and the receiving waters of Humboldt Bay were used to reevaluate the effluent limitations for copper at Discharge Point 001. These new water quality-based effluent limitations (WQBEL) will be recommended to the Regional Water Quality Control Board, at which time an agreement must be reached between the Water Board and the City of Eureka. The agreement will include the adoption of new effluent limitations for copper that will be documented in the new NPDES permit.

The calculation of new WQBELs for an ocean discharge includes the consideration of the water quality criterion, dilution credit and ambient concentration at the site.[9] The basis of the WQBEL is the priority pollutant objective, or aquatic life objective, which has a default value for the WER of 1.0. If a discharger conducts the appropriate analysis to show that the WER has a value different than 1.0, then a new site-specific objective (SSO) can be calculated.

The criterion maximum concentration (CMC) and criterion continuous concentration (CCC) are used as water quality objectives to express concentrations reaching acute and chronic thresholds, respectively, for marine environments (Eqn 3).

$$\textit{Site-Specific Objective} = \textit{Water Quality Objective} \bullet \textit{Final WER} \qquad \text{(Eqn 3)}$$

The current national saltwater CMC and CCC for dissolved copper are 4.8 and 3.1 µg/L, respectively.[6] Discharge Point 001 at Elk River WWTF is regulated as an ocean discharge with respect to copper, and the more stringent water quality objectives are used to calculate the WQBELs. For this reason, the value of 3.1 µg/L is used for calculating the effluent limitations. The WQBEL values for copper are expressed as the total recoverable metal in the expired NPDES permit (Table F-11 and F-12).[1] This conservative approach ensures that marine life is protected.

Both the fWER values for the undiluted effluent at Discharge Point 001 and the receiving waters of Humboldt Bay need to be considered when determining the new site-specific objective. The fWER of 12.6 for undiluted effluent shows that the copper in the wastewater is not bioavailable, and that the water contains excess dissolved organic matter that can bind free or labile copper that may otherwise be toxic to sensitive species. Although this is reassuring, the fWER for the receiving waters was 1.3, which shows less of an ability to buffer against any addition of bioavailable copper. For this reason, a conservative approach is taken, and it is recommended that the WER default value of 1.0 be changed to 1.3. This allows for a new site-specific objective to be calculated using Eqn 3:

Site-Specific Objective = 3.1 µg/L • 1.3 = ***4.0 µg/L****.*

Under the *California Ocean Plan* the WQBELs are calculated using equation 4:

$$C_e = C_o + D_m\,(C_o - C_s) \qquad \text{Eqn 4}$$

where:

C_e = the effluent limitation in mass concentration units of µg/L
C_o = the concentration to be met after dilution, currently using the CCC with a value of 3.1 µg/L
C_s = background seawater concentration with a default value of 2 µg/L for copper[9]
D_m = minimum probable initial dilution expressed as parts seawater per part wastewater with a current dilution credit value of 30.

The results from the copper WER study modify the C_o value by substituting in the new SSO = 4.0 µg/L for the CCC = 3.1 µg/L (Eqn 3 and 4). Note that the fWER, the calculated effluent limitation (C_e), and the background seawater concentrations (C_s) are expressed in the total recoverable copper fraction. However, the water quality objective, or CCC, is a dissolved copper criterion. The SSO was calculated with the more stringent dissolved copper water quality objective and a fWER representing the total recoverable fraction.

Without a current NPDES permit for guidance in calculating new effluent limitations, the expired Elk River WWTF NPDES permit and the *California Ocean Plan* were used to calculate the following effluent limitations:

(6-month median) $C_e = 4 + 30\,(4 - 2) = 64\ \mu g/L$

(daily maximum) $C_e = 16 + 30\,(16 - 2) = 436\ \mu g/L$

(instantaneous maximum) $C_e = 40 + 30\,(40 - 2) = 1180\ \mu g/L$

These new WQBELs for copper are based on the evidence in this study that the WER value at the site of discharge was different than the default value of 1.0. It is recommended that these new effluent limitations be applied to the new NPDES permit upon approval by the Regional Water Quality Control Board. However, it is also recommended that if Elk River WWTP discharge of copper has not exceeded these new limitations during previous monitoring at Discharge Point 001 then there is evidence that copper poses no reasonable potential in harming sensitive species in the receiving waters and an effluent limit for copper is not necessary.

4. REFERENCES

1. California Water Boards: Regional Water Quality Control Board, North Coast Region. National Pollutant Discharge Elimination System (NPDES) Permit Order No R1-2009-0033 for the City of Eureka, June 2009.

2. U.S. EPA: Ambient Water Quality Criteria for Copper; Tables. USEPA Office of Water, EPA-822-R-03-026, November 2003.

3. Sunda, William G.; Guillard, Robert. R. L. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. Journal of Marine Research, 1976, 34, 511-529.

4. Brand, Larry E.; Sunda, William G.; Guillard, Robert R.L.. Reduction of marine phytoplankton reproduction rates by copper and cadmium. Journal of Experimental Marine Biology, 1986, 96, 225-250.

5. Bruland, K.W. and M.C. Lohan. The control of trace metals in seawater. Chapter 2 in *The Oceans and Marine Geochemistry*, Vol. 6 (Ed. Harry Elderfield) in Treatise on Geochemistry (Eds. H.D. Holland and K.K. Turekian), 2004.

6. U.S. EPA: Streamlined Water-Effect Ratio Procedure for Discharges of Copper. USEPA Office of Water, EPA-822-R-01-005, March 2001.

7. U.S. EPA: Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California. Federal Register, Vol. 65, No. 97, May 2000.

8. State Water Resources Control Board. Policy for Implementation of Toxics Standard for Inland Surface Waters, Enclosed Bays, and Estuaries of California. California Environmental Protection Agency, 2005.

9. California Ocean Plan. California Environmental Protection Agency, 2012.

10. Barnhart, R.A, M.J. Boyd and J.E. Pequegnot. Ecology of Humboldt Bay, California: An Estuarine Profile. U.S. Fish and Wildlife Service Biological Report 1, 1992, pg. 18.

11. U.S. EPA: Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Criteria Levels, USEPA Office of Science and Technology, EPA-823-B-94-001, April 1995.

12. Donat, J.R., K.A. Lao and K.W. Bruland. Speciation of dissolved copper and nickel in South San Francisco Bay: A Multi-method approach. Analytica Chimica Acta, 1994, 284, 557-572.

13. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 1998.

14. U.S. EPA: Use of Water-Effect Ratios and the Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms, USEPA Office of Water, EPA-821-R-02-012.

Appendix 1