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FINAL REPORT

Los Angeles River Copper Water-Effect Ratio (WER) Study

Prepared for:
City of Los Angeles Regulatory Affairs Division
City of Burbank

Prepared by:
Larry Walker Associates – Santa Monica, California

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Note: Cover photographs from left to right are of the Los Angeles River immediately downstream of the L.A. Glendale Water Reclamation Plant and immediately downstream of the Tillman Water Reclamation Plant during dry weather conditions.

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GLOSSARY OF ACRONYMS, ABBREVIATIONS, & CHEMICAL SYMBOLS

B1	Burbank Water Reclamation Plant Effluent Sampling Site
BLM	Biotic Ligand Model
BWRP	Burbank Water Reclamation Plant
CCC	Criterion Continuous Concentration
cfs	Cubic Feet Per Second (measure of flow)
CMC	Criterion Maximum Concentration
Cu	Copper
CWA	Clean Water Act
CTR	California Toxics Rule
DCTWRP	Donald C. Tillman Water Reclamation Plant
DIC	Dissolved Inorganic Carbon
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EC	Electrical Conductivity
EC50	50% Effect Concentration
EDW	Effluent Dependent Waterbody
FACR	Final Acute-Chronic Ratio
FDPE	Fluorocarbon-lined High-Density Polyethylene
fWER	Final Water-Effect Ratio
G1	Los Angeles-Glendale Water Reclamation Plant Effluent Sampling Site
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma – Mass Spectrometer
LAGWRP	Los Angeles-Glendale Water Reclamation Plant
LARA	Los Angeles River downstream of Arroyo Seco – flow gage
LARR	Los Angeles River at Rosecrans – sampling site
LART	Los Angeles River downstream of Tujunga – flow gage
LARW	Los Angeles River at Willow – sampling site Los Angeles River at Wardlow – flow gage
LC50	50% Lethal Concentration
LOEC	Lowest Observable Effect Concentration
LWA	Larry Walker Associates
MCO	Modified Copper Water Quality Objective
MGD	Million Gallons Per Day
mg/L	Milligrams Per Liter (aka: ppm, parts per million)
MSD	Minimum Significant Difference
ng/L	Nanograms Per Liter (aka: ppt, parts per trillion)
NOEC	No Observable Effect Concentration
NPDES	National Pollutant Discharge Elimination System
ORD	Office of Research and Development
PER	Pacific EcoRisk Environmental Consulting and Testing
POTW	Publicly-owned Treatment Works
ppt	Parts Per Thousand (Salinity)
QA/QC	Quality Assurance/Quality Control
R4	Los Angeles-Glendale Water Reclamation Plant Receiving Water Sampling Site

GLOSSARY - continued

RPD	Relative Percent Difference
RWQCB	Regional Water Quality Control Board (Los Angeles Region)
SC	Stakeholder Committee
SIP	State Implementation Policy
SOP	Standard Operating Procedures
SSO	Site-Specific Objective
sWER	Sample Water-Effect Ratio
SWRCB	State Water Resource Control Board
T1	Donald C. Tillman Water Reclamation Plant Effluent Sampling Site
TAC	Technical Advisory Committee
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
TSS	Total Suspended Solids
ug/L	Micrograms Per Liter (aka: ppb, Parts Per Billion)
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
W1	Los Angeles River at Los Feliz Bridge – sampling site
WER	Water-Effect Ratio
WQC	Water Quality Criteria
WQO	Water Quality Objective
WWTP	Wastewater Treatment Plant

1 INTRODUCTION

1.1 BACKGROUND

1.1.1 USEPA Water-Effect Ratio Protocols and Procedures

The US Environmental Protection Agency (USEPA) publishes national water quality criteria (WQC) for the protection of aquatic life consist of a concentration, an averaging period and a return frequency. In 1994, USEPA published detailed protocols for adjusting the concentration portion of its national metals WQC to reflect site-specific receiving water conditions using the "Water-Effect Ratio" (WER) method, referred to as the "Interim Guidance" (USEPA 1994). The Water-Effect Ratio[1] method requires rigorous parallel toxicity tests using USEPA-specified laboratory water and "site water" to determine whether physical and chemical characteristics in the site water affect the bioavailability and, therefore, the toxicity of copper to aquatic organisms. Site water is generally used to describe receiving water, effluent, or simulated downstream water. Simulated downstream water is site water prepared by mixing upstream receiving water and effluent in a known ratio. The difference in toxicity values is expressed as a WER (the EC50[2] endpoint obtained in the site water divided by the EC50 endpoint in the lab water). A WER is expected to account for (a) the site-specific toxicity of a metal and (b) synergism, antagonism, and additivity with other constituents present in the site water (USEPA 1994).

In March 2001, the USEPA published a streamlined national procedure for developing a WER for copper in freshwater bodies (USEPA 2001). Because of the numerous copper WER studies that have been performed throughout the country since the mid-1990s, the USEPA determined there were sufficient data to develop a more straightforward testing approach for situations where copper concentrations are elevated primarily by continuous point source effluents - such as a POTW outfall. This USEPA protocol, referred to as the "Streamlined Procedure" in this report, specifies sample collection method, lists the species and analyses to perform, requires toxicity tests on only one aquatic species, and reduces the number of samples to be collected relative to the USEPA's 1994 *Interim Guidance* document.

1.1.2 Purpose and Uses of a Water-Effect Ratio

The WER is a factor that can be used under the USEPA's system of WQC to customize national aquatic life criteria, which include California Toxic Rule (CTR) aquatic life criteria established by USEPA in 2000, to reflect site-specific water column conditions. The WER is used to derive site-specific criteria that maintain the level of protection of aquatic life intended by the "Guidelines for deriving numerical national WQC" (USEPA 1985). If the value of the WER exceeds 1.0, the site water reduces the toxic effects of the pollutant being tested. Conversely, the WER can be less than 1.0, in which case the toxic effects of the pollutant in site water would be greater than that in laboratory water and the site-specific WQC should be less than the WQC. The site-specific acute and chronic USEPA criteria are calculated by multiplying the USEPA's ambient WQC values by a locally developed WER.

The WER connects copper WQC to beneficial uses. A copper WER developed for specific reaches of the Los Angeles River (L.A. River), if approved by state and federal water quality regulatory agencies [the Los

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[1] A WER is used to determine whether physical and chemical characteristics in site water affect bioavailability and toxicity of copper to aquatic organisms. WER = Species EC50 in site water ÷ Species EC50 in laboratory water.

[2] EC50 = 50% Effect Concentration = Concentration which adversely affects 50% of test species.

Angeles Regional Water Quality Control Board (RWQCB)/State Water Resources Control Board (SWRCB), and USEPA Region 9, respectively], may be used in the future to:

- evaluate 303(d)-list copper impairment status of the L.A. River,
- conduct Reasonable Potential Analyses (RPA) for copper, and
- calculate maximum allowable copper concentrations in effluent for National Pollutant Discharge Elimination System (NPDES) permits such that aquatic life in the L.A. River will be protected.

There are three major publicly owned wastewater treatment works (POTWs) that discharge tertiary effluent into the L.A. River: the Donald C. Tillman Water Reclamation Plant (DCTWRP), the Los Angeles-Glendale Water Reclamation Plant (LAGWRP), and the Burbank Water Reclamation Plant (BWRP). Receiving water data collected in different parts of the country have shown that waterbodies where POTW discharges constitute a large proportion of flow tend to have higher concentrations of organic material and sediment than laboratory dilution water used for toxicity tests supporting USEPA's national copper WQC (see Appendix 1). This organic material has been shown to mediate copper toxicity to aquatic organisms. As a result, USEPA and CTR copper WQC based on total or dissolved copper may be more conservative than intended by USEPA in estimating the maximum allowable concentration to protect aquatic life.

1.2 STUDY OBJECTIVE

The purpose of this Study, which is sponsored by the Cities of Los Angeles and Burbank, is to determine the WER for copper in the L.A. River downstream of the discharges of each of three POTWs – two operated by the City of Los Angeles and one operated by the City of Burbank. As mentioned previously, the WER connects copper WQC to beneficial uses. The beneficial use of aquatic life habitat is protected from copper toxicity when copper WQC are attained. The WER connects the default national WQC to site-specific conditions (copper binding capacity) that also affect beneficial use of aquatic life habitat. It is important to know what copper concentrations in the L.A. River are protective of aquatic life. National WQC are based on toxicity data generated using laboratory dilution water. The WER, a protocol developed by USEPA, will convert national WQC for copper to site-specific objectives based on observed toxicity in the L.A. River itself, rather than in laboratory dilution water. Figure 1 presents the study area.

A WER of 1.0 means that copper toxicity in dilution water used in toxicity tests to derive the national WQC is the same as copper toxicity in effluents diluted by the L.A. River. If the WER is less than 1.0, then the site-specific copper WQC for the L.A. River should be set at a concentration lower than the national WQC. If the WER is greater than 1.0, then CTR copper WQC are lower than what is required to be protective for aquatic life in the L.A. River. Therefore, the copper site-specific objective (SSO) for the L.A. River may be set at a higher concentration than the national WQC and still be protective of aquatic life beneficial uses.

Alternative to adopting a SSO, Los Angeles Regional Water Quality Control Board (Regional Board) staff has indicated they may incorporate the information as implementation provisions to the CTR copper criteria as modified copper water quality objectives (MCO). The WER(s) determined in this Study will support modification of the regional copper criteria, as authorized in the CTR. The MCO can be formally added by the RWQCB, with the approval of the SWRCB and USEPA, to the "Water Quality Control Plan: Los Angeles Region Basin Plan for the Coastal Watersheds of Los Angeles and Ventura Counties" (Basin Plan) adopted by the LARWQCB in 1994. Alternatively, in accordance with the "Policy for Implementation of Toxic Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California" (State Implementation Policy, or SIP) amendments approved by the SWRCB in February 2005, the WER can be utilized directly in future NPDES permit renewals as a site-specific modification to CTR copper WQC.

Figure 1. L.A. River Copper WER Study Area

The primary goals of this Study include:

1. Determine appropriate copper WERs for the L.A. River.
2. Support a regional approach for determining copper WERs and SSOs.
3. Collect data to evaluate use of the Biotic Ligand Model (BLM) to predict copper toxicity in the L.A. River.

In attempting to address the first goal of the Study, determining appropriate WERs, four key questions were identified:

- Is dry weather the critical condition for copper in the L.A. River?
- Are there differences in WERs between reaches of the L.A. River?
- If there are differences in WERs between reaches of the L.A. River, are any reaches similar?
- Are upstream WERs sufficiently protective of downstream aquatic life beneficial uses as intended by the CTR copper criteria?

These questions are addressed in various sections of this report.

A preliminary WER Study completed by the City of Los Angeles in July 2003 (LWA 2003) for dry weather conditions showed that a WER using USEPA protocols may be successfully determined for the L.A. River. Preliminary results suggest that the WER is higher than 1.0. In other words, CTR copper WQC appear to provide a higher level of protection for aquatic life than intended by USEPA criteria. To support the community's long-term vision of enhanced habitat in the L.A. River, it is essential to establish WQC that accurately reflect beneficial uses. The results from this Study will ultimately help the community set priorities for different implementation actions, such as stream habitat enhancement, Best Management Practices (BMPs) to reduce urban runoff copper loads, and POTW upgrades if necessary to comply with the MCOs.

Additionally, this Study will support a regional approach for determining copper WERs and SSOs/MCOs. A work plan was developed for evaluation of the copper WER in the San Gabriel and Dominguez Channel watersheds (CEPRD 2004). The Southern California Coastal Water Research Project (SCCWRP) agreed to be the lead on that work plan. The San Gabriel and Dominguez Channel plan proposed a combined approach for developing regional copper SSOs that utilizes WER testing and data collection for validation of the BLM for the region's waterbodies. Although the San Gabriel / Dominguez Channel work plan has not been implemented at the time of this report, it is important that the approach in the L.A. River Copper WER Study complement the goals of the San Gabriel / Dominguez Channel study, and that the results of these studies can be evaluated in a common forum to develop a consistent conceptual model for the linkage between dissolved copper, local water conditions, and beneficial uses. Coordination of these and other upcoming WER studies in the Los Angeles Region will promote efficiency and consistency in the Basin Planning process for copper SSOs/MCOs.

2 APPROACH

In the July 12, 2004 draft L.A. River Copper WER Work Plan (LWA 2004), the scope of WER sampling during dry weather conditions was planned using the approach presented in the Streamlined Procedure. However, to address stakeholder comments on the applicability of the Streamlined Procedure to the L.A. River, the number of sampling events during dry weather conditions (considered the critical conditions) was increased from the two events recommended in the Streamlined Procedure. Also, additional WER testing was conducted for both wet and dry winter conditions to determine whether dry or wet weather conditions result in WERs most appropriate for water quality conditions in the L.A. River, resulting in four dry and one wet weather event for a total of five events. A further significant change to the July 12, 2004 Work Plan was the addition of two WER sampling stations in the lowest freshwater reaches of the L.A. River (20 and 26 miles downstream of the LAGWRP) to determine if urban runoff between these sites and the upper reaches (Figure 1) causes alterations in the copper WER. The Technical Advisory Committee (TAC) supported these revisions to the July 12, 2004 Work Plan and continuation of the use of a single test species, *Ceriodaphnia dubia* (*C. dubia*). The protocol being applied in this Study can best be described as an "enhanced" Streamlined Procedure since it has an enhanced number of sampling events and includes extra temporal and spatial testing to verify that dry season conditions yield conservative WERs. The Final Work Plan ("Work Plan for a Copper Water-Effect Ratio Study for the Los Angeles River [2005])", included in Appendix 2, summarizes the rationale for selecting sampling sites, monitoring and analytical procedures, and quality assurance/quality control (QA/QC) protocols.

Copper toxicity tests with a single sensitive species (*C. dubia*) were used to develop EC50 data for WER calculations for segments of the L.A. River below each of the three POTWs covered by this Study as well as in the lower freshwater reaches. WER samples were collected from both POTW effluent and the L.A. River, during both dry season and wet season flow conditions, and in wet and dry conditions during the wet season. Section 3.1 (Sample Collection Sites and Schedule) discuss the sampling sites and schedule in more detail.

The acute toxicity test methods used in this study met the highest quality requirements for use in deriving national WQC as listed in the National WQC Guidelines. In this Study, side-by-tests were conducted to compare the toxicities of copper in site water and lab water spiked with copper. Copper concentrations used in site water and lab water tests differed because the toxicity of copper in lab water was greater than the toxicity of copper in site water because copper binding in site water was greater. Additionally, samples were collected to assist in developing the BLM (discussed in more detail immediately below) and to assess two potential areas of concern:

1. The potential for chemical and water quality parameters concentrations to vary over the duration of a 24-hour composite collection. Chemical parameters measured as part of this assessment included parameters likely to affect the bioavailability of copper (dissolved organic carbon and hardness as $CaCO_3$), general parameters (specific conductance, pH, dissolved oxygen), and total and dissolved copper. Concern was expressed by the TAC that collection of samples as 24-hour composites could lead to variability in chemical parameters that affect the bioavailability of copper and could subsequently affect the resulting WER toxicity tests. Results of the variability analysis are presented in section 6.1.

2. The possible effects of a wet weather "shoulder event" on copper toxicity. The term "shoulder event" term is used in this report to describe elevated base flows in the L.A. River resulting from dam releases following storm events. A "shoulder event" is defined as a period of at least 5 consecutive days in which the flow rate is within the 75th and 90th percentiles of flows measured at the Firestone Blvd gauging station (178 cfs and 414 cfs, respectively). Concern was expressed by the stakeholder group that "shoulder event" conditions could represent the critical condition for copper bioavailability in the L.A. River. Results of the "shoulder event" analysis are summarized in section 6.2.

Four specialized environmental testing laboratories conducted analytical work on water samples collected for this Study:

- Pacific EcoRisk (PER) Environmental Consulting and Testing, Martinez CA, conducted acute toxicity tests for copper. PER specializes in toxicity testing of this nature and has successfully completed a copper WER study for a coalition of NPDES permittees in the San Francisco Bay region.
- CRG Marine Laboratories, Inc. (CRG), Torrance CA, performed analyses for low-level dissolved copper and total suspended solids (TSS) as required for laboratory and site water tests.
- Calscience Environmental Laboratories, Inc (Calscience) in Garden Grove CA, conducted analyses of additional water quality constituents.
- Aquatic Bioassay and Consulting (ABC) Laboratories in Ventura CA, conducted analyses of particle size distribution.

These laboratories are certified by the California Department of Health Services-Environmental Laboratory Accreditation Program (DHS-ELAP) to perform all analyses, in conformance with USEPA and California requirements.

2.1 BIOTIC LIGAND MODEL

The BLM was developed by HydroQual Inc. to evaluate bioavailability and toxicity of metals that are discharged into surface water. The BLM considers several water quality constituents, including hardness, dissolved organic carbon (DOC), chloride, pH, and alkalinity. USEPA released the revised "Aquatic Life Ambient Freshwater Quality Criteria – Copper" (Copper Criteria Guidance) based utilizing the BLM in February 2007. The Copper Criteria Guidance does not constitute regulation and is intended to provide updated guidance to states for establishing water quality standards. Water quality constituents required as inputs for the BLM were collected as part of this Study to provide useful data to BLM researchers, to ensure data may be used in the BLM, and to investigate the applicability of the BLM to this and similar WER studies.

2.2 CHEMICAL ANALYSIS

The primary emphasis of this Study is the development of copper WERs. However, additional water chemistry and general parameter data were collected for use in the BLM and to further characterize the receiving water. Additional analysis included:

- Total and dissolved copper
- Total hardness as $CaCO_3$
- Total suspended solids (TSS)
- Dissolved organic carbon (DOC)
- Dissolved inorganic carbon (DIC)
- Potassium
- Magnesium
- Calcium
- Sodium
- Chloride
- Sulfate
- Total sulfide
- Alkalinity
- pH
- Conductivity
- Salinity
- Temperature
- Dissolved oxygen

2.3 PUBLIC PARTICIPATION PLAN

Technical review and public participation for this Study consisted of two components. The first was the review of work progress, Work Plan, and the final Study report by the TAC and a stakeholder committee (SC). The second component is public participation and comments solicited through public workshops. The TAC consists of outside experts who have conducted independent peer review of various versions of the Work Plan, data, and study conclusions presented in this report. Table 1 provides a list of the TAC members.

The SC, formed by RWQCB staff, includes a staff member from the RWQCB, the SWRCB, USEPA Region 9, California Department of Fish and Game, US Fish and Wildlife Service, the City of Los Angeles, the City of Burbank, and local environmental/public interest groups. The SC served as the primary stakeholder body for review of the Work Plan, and will review the analytical results and study conclusions presented in this report. The TAC will provide independent peer review of any technical recommendations from the SC.

Table 1. L.A. River Copper WER Study Technical Advisory Committee

Member	Agency/Company	Expertise
Charles Alpers	USGS	Well-known expert on trace metal chemistry in natural waters, and has served on other TACs.
Gary Chapman	Paladin Consulting	Former USEPA ORD employee. Expert in freshwater aquatic toxicology and WQC development (including development of the Interim Guidance)
David Hansen	HydroQual Inc.	Former USEPA ORD employee. Expert in marine aquatic toxicology and WQC development (including development of the Interim Guidance).

The TAC and SC participated in review and comment on several versions of the Work Plan. The TAC reviewed and submitted comments on the June 10, 2004 version of the Work Plan. Responses were developed for the TAC comments and changes were incorporated into the July 12, 2004 draft Work Plan which was presented to the SC at a workshop on July 22, 2004. Based on SC comments on the July 12, 2004 draft Work Plan and a L.A. River site visit by the TAC on February 14, 2005, additional comments from the TAC were received by the Study sponsors during the week of February 21, 2005. Based on input by the SC and TAC through February 2005, the Study sponsors decided in May 2005 to expand the scope of the Study to include an additional sampling event for all stations and to add two downstream sampling stations in the lower freshwater reach of the L.A. River. Written comments on the June 30, 2005 draft Work Plan were incorporated into the Final Work Plan (10/18/05 – See Appendix 2). Verbal comments on issues not related to sampling were received during the September 8, 2005 SC meeting and were incorporated into the Final Work Plan (10/18/05 – See Appendix 2). The intent of these changes was to increase confidence in determining scientifically accurate, precise and protective copper WERs for the L.A. River.

3 ENVIRONMENTAL SETTING

The L.A. River and its tributaries are located in Los Angeles County, California. The L.A. River drains approximately 843 square miles. The main surface water system drains from the San Gabriel Mountains in the northeast and the Santa Monica Mountains in the northwest toward the southeast where it flows through highly urbanized areas (including the City of Los Angeles) before emptying into the Pacific Ocean through the estuary. The Santa Susana Mountains and Santa Monica Mountains form the northwestern boundary of the watershed, while the eastern boundary is formed by the San Gabriel Mountains. Land uses in the L.A. River watershed can be generally categorized as forest, agriculture, high- and low-density residential, commercial, industrial, and open space. The current land use in the watershed is approximately 54% urban and 44% forest/open space, with the remaining comprised of agriculture, water and other land uses. For a more comprehensive description of the L.A. River watershed, see the L.A. Rivers Metals TMDL Environmental Setting section (LARWQCB 2005) presented in Appendix 3.

3.1 SAMPLE COLLECTION SITES AND SCHEDULE

Seven WER sampling sites were used to represent four reaches and one tributary of the L.A. River (Figure 2). Additionally, a sample was collected at the spill way of Hansen Dam on Tujunga Wash, approximately nine miles upstream of its confluence with the L.A. River, to provide data for evaluating “shoulder event” conditions. Five WER sampling events were conducted between August 2005 and March 2006. Sample collection to assess composite sample degradation occurred in July 2005 and sample collection to assess the “shoulder event” occurred in April 2006. Table 2 presents the WER sampling schedule. Events 1, 2, and 3 targeted dry weather during the dry season with composite samples collected over a 24-hour period. Event 4 targeted wet weather during the wet season with grab samples collected over a 12-hour period matching the hydrograph and composited into a single sample. Lastly, Event 5 targeted dry weather during the wet season with composite samples collected over a 24-hour period. Appendix 4 contains pictures of WER sampling sites.

Table 2. L.A. River Copper WER Sampling Schedule

Sampling Site	Site ID	Sample ID Used in Tables and Figures	L.A. River Reach #	Dry Season Dry Weather: Planning Event[1] July 20 2005	Dry Season Dry Weather: Event 1 Aug 16/17 2005	Dry Season Dry Weather: Event 2 Sept 19/20 2005	Dry Season Dry Weather: Event 3 Oct 5/6/7 2005	Wet Season: Event 4 Wet Weather Feb 27/28 2006	Wet Season: Event 5 Dry Weather Mar 26/27 2006	Wet Season: Shoulder Event Conditions Apr 5 2006
DCTWRP Effluent	T1	T1	5		X	X	X	*Not sampled for wet season events*		
BWRP Effluent	B1	B1	BWC		X	X	X			
Upstream of LAGWRP, River[2]	R4	SDW[2]	3	O	X	X	X			
LAGWRP Efflent[2]	G1		3							
Los Feliz Bridge, River	W1	W1	3	*Not sampled for dry season events*				X	X	
Rosecrans Ave, River	LARR	LARR	2		X	X	X	X	X	
Willow Street, River	LARW	LARW	1		X	X	X	X	X	
Laboratory Water	Lab Water	Lab Water	NA		X	X	X	X	X	
Hansen Dam	Hansen Dam		NA							O

BWC = Burbank Western Channel (discharges to Los Angeles River Reach 4)
O – Represents dates and locations where only chemical analyses were performed.
X – Represent dates and locations where both toxicity tests and chemical analyses were conducted. Both toxicity tests and chemical analysis were conducted on lab water.
NA – Not applicable
1 The Planning Event was not a complete sampling event. It was intended for planning subsequent events and the special variability test samples per TAC suggestion at LAGWRP receiving water site R4.
2 These two samples were combined to create a simulated downstream water (SDW) sample using 7Q10 approach [per Streamlined Procedure] to form a single sample for Events 1 through 3.

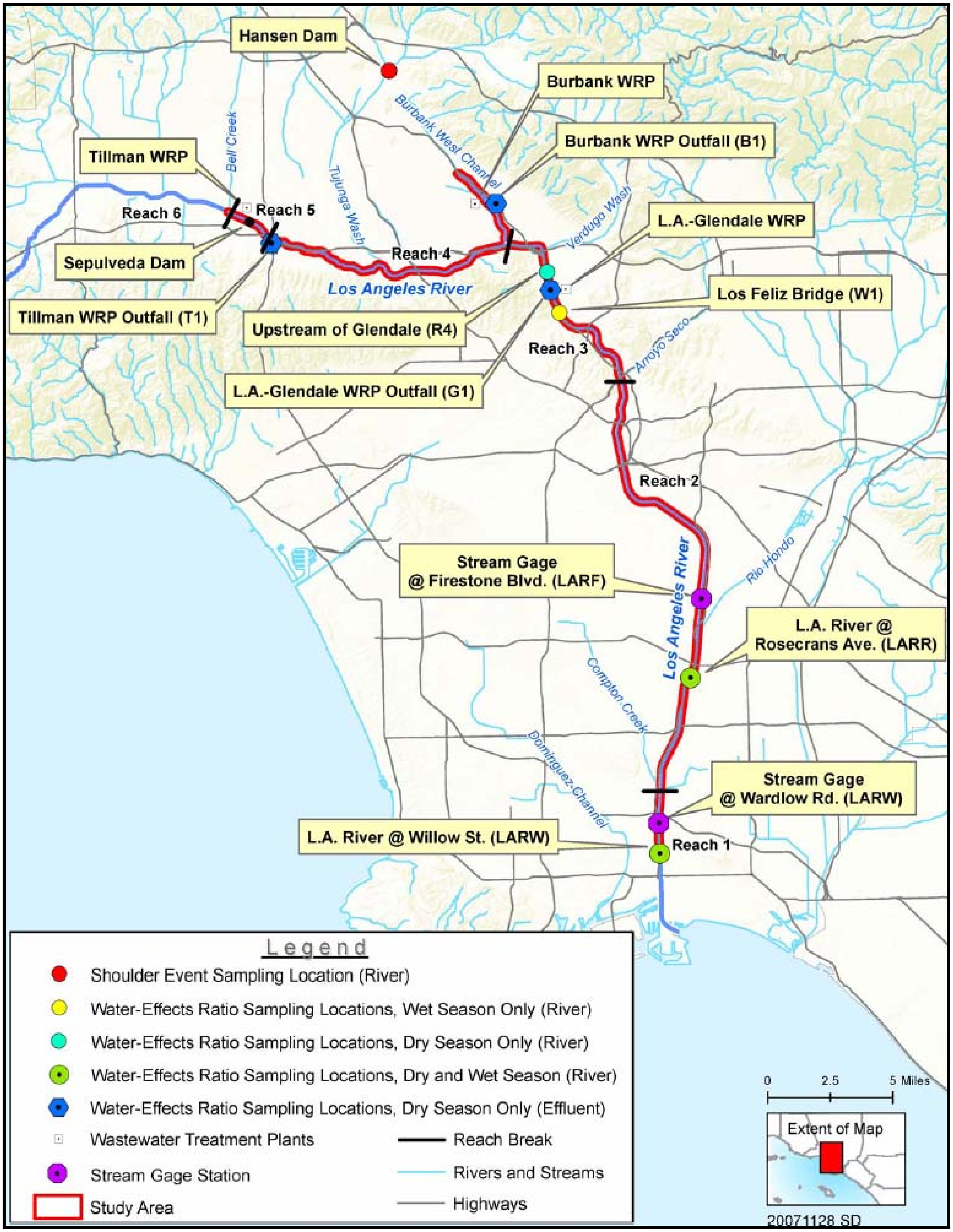

Figure 2. Map of L.A. River Copper WER Monitoring Stations and Wastewater Reclamation Plant Discharge Locations

3.2 SAMPLE COLLECTION PROCEDURES FOR SIMULATED DOWNSTREAM SAMPLES

USEPA's Interim Guidance and Streamlined Procedure applicable to POTW-dominated WERs specifies use of simulated downstream water as the site water for the Study. The simulated water (site water) is created by mixing upstream receiving water with treated effluent at a ratio corresponding to the design low-flow conditions of the receiving water (upstream of the outfall) and the permitted design discharge capacity of the POTW.

Because the December 2004 SCCWRP draft Copper WER work plan for the San Gabriel River and Dominguez Channel utilizes a stratified random spatial composite sampling strategy, this approach was considered for this Study. A stratified random sampling strategy would be consistent with SCCWRP's work plan and with the approach recommended in USEPA's 1996 translator guidance (USEPA 1996). In the SCCWRP study work plan, it was concluded that stratification and randomized sampling would be necessary to account for heterogeneity in each waterbody segment and to ensure the collection and testing of representative samples. However, after evaluating the hydrological characteristics of the L.A. River under dry weather critical low flow conditions, it was concluded that spatial composite sampling would provide little or no additional information about potential variability of WERs in the L.A. River. Under the low flow critical sampling conditions defined for the Study, the L.A. River in the vicinity of the three POTWs is comprised principally of effluent with very little other flow (urban runoff) and, therefore, little spatial heterogeneity is expected. WER testing and analysis of BLM parameters in simulated downstream water will provide results that are comparable and compatible with the SCCWRP approach and will support the objectives of that study. Furthermore, the TAC confirmed that simulated downstream water approach specified by the Streamlined Procedure is suitable for this Study.

3.2.1 Sample Collection for the LAGWRP

The L.A. River directly upstream of the LAGWRP outfall has consistent measurable flows in dry weather conditions due to tertiary effluent discharges from the upstream DCTWRP and BWRP. Twenty-two years of dry weather flow data are available from the Army Corps of Engineers gage upstream of the LAGWRP.[3] For the LAGWRP copper WER determination, a mixture of upstream L.A. River water and LAGWRP effluent, prepared according to the Streamlined Procedure, was used for the site water. The chosen ratio of upstream water to LAGWRP effluent is based on the dilution ratio guidance in the SIP for the CTR. Additionally, this approach is consistent with the Streamline Procedure, which states that effluent and upstream samples are to be combined at the dilution corresponding to the design low flow condition that the permitting authority uses in permit limit calculations.

For chronic aquatic life criteria, the 7Q10 upstream flow (lowest seven-day average flow that occurs with a statistical frequency of once every 10 years during the 22-year analysis period) is the critical low-flow condition outlined in the SIP for establishing permit limits. For this reason, the 7Q10 upstream flow was used to create the LAGWRP simulated downstream water sample at design low-flow conditions. For the LAGWRP, the quantity of effluent discharged to the L.A. River was set as the dry weather design capacity of the treatment plant of 20 MGD. Following the critical low-flow conditions outlined in the SIP was intended to be conservative. This choice may have had the opposite effect if the effluents had different

[3] This represents the period subsequent to the DCTWRP coming on line in 1983.

characteristics. For example, if the WERs for DCTWRP and/or BWRP were lower than the WER for LAGWRP, then minimizing upstream flow and maximizing LAGWRP effluent flow would have high biased the WER. As it turns out the WERs, presented in later sections of the report, are such that use of the 7Q10 results in conservative estimates of WERs. The method and calculations for preparing the LAGWRP site water mixture are discussed below.

A composite sampler was temporarily installed to collect hourly aliquots at the LAGWRP effluent monitoring station over a 24-hour period. After the 24-hour period, field staff used a portion of each aliquot based on each hour's proportion of total flow over the 24-hour sampling period to create a flow-based composite sample. The composite samplers were prepared for clean metals sampling and packed with ice to preserve sample integrity. After creating manually composite samples, the samples were shipped for next morning delivery to Pacific EcoRisk.

Upstream receiving water samples for LAGWRP were collected approximately 220 feet upstream of the LAGWRP discharge point, near the City's NPDES receiving water monitoring station "R4". The upstream L.A. River samples at R4 were collected as 2.5 or 3-gallon grab samples every six hours for a 24-hour period (coincident with the effluent composite collection period) and flow proportioned volumes were then mixed together in a 5-gallon container to form a 5-gallon manually composited upstream sample. Samples were collected at mid-depth as close to a point of significant flow as could be safely reached by the sampling crew.

The LAGWRP simulated downstream water sample was prepared by the sampling crew at the DCTWRP laboratory facilities. Simulated downstream water, in accordance with the Streamlined Procedure, was created by combining water from the upstream composite receiving water sample (R4) and the composite effluent sample in a predetermined ratio. The ratio for LAGWRP toxicity testing sample preparation was determined using the design low-flow condition for the L.A. River represented by the 7Q10 flow in the upstream water and the design capacity for the LAGWRP. Table 3 summarizes the simulated downstream water ratio calculations for LAGWRP.

Table 3. LAGWRP Simulated Downstream Water Mixing Volumes

Water Type	Flow (MGD)	Percent of Simulated Downstream Water	Volume for Simulated Downstream Water (gallons)
7Q10 Upstream[1]	16.6	45.4%	2.27
LAGWRP discharge	20[2]	54.6%	2.73
Simulated water sample	36.6	100%	5.00

1 See Appendix C of the Final Work Plan for calculation of the River 7Q10 flow upstream of the LAGWRP.
2 Permitted design average dry weather flow for the LAGWRP

Composited upstream water (2.27 gallons) from the 5-gallon container was thoroughly mixed and poured directly into a 5-gallon container containing 2.73 gallons of LAGWRP composited effluent to create a composited 5-gallon simulated 7Q10 flow site water sample. After compositing, the samples were shipped for overnight delivery to Pacific EcoRisk.

3.2.2 Sample Collection for the DC Tillman and Burbank WRPs

The City of Los Angeles receives no dilution credit for the two POTWs it operates on the L.A. River. However, flow is usually present in the L.A. River upstream of the DCTWRP during dry weather, but is very small compared to typical DCTWRP discharge. Due to the low flows involved, there are no reliable historical dry weather flow measurements in the L.A. River directly upstream of the DCTWRP discharge with which to calculate the 7Q10 value. Therefore, the WER site water sample for the DCTWRP consisted of 100% tertiary effluent from the DCTWRP outfall. This approach is consistent with the zero dilution credit specified in the NPDES permit for DCTWRP.

The BWRP discharges to the Burbank Western Wash, which is a concrete-lined flood control structure tributary to the L.A. River between DCTWRP and the LAGWRP. Based on discussions in October 2003 with City of Burbank staff, there is minimal, if any, dry weather flow in the Burbank Western Wash upstream of the BWRP outfall 002[4]. Since there are no gaging stations in the Burbank Western Wash upstream or downstream of the BWRP discharge point, an assumption was made for the purposes of this Study, that the 7Q10 value for the Burbank Western Wash upstream of the BWRP outfall 002 is zero. This approach is consistent with the zero dilution credit specified in the NPDES permit for BWRP. In accordance with the Streamlined Procedure, simulated site water for development of a BWRP copper WER using this option, consisted of 100% effluent from outfall location 002.

A composite sampler was temporarily installed to collect hourly aliquots at the DCTWRP and BWRP effluent monitoring stations over a 24-hour period. After the 24-hour period, field staff used a portion of each aliquot based on each hour's proportion of total flow over the 24-hour sampling period to create a flow-based composite sample. The composite samplers were prepared for clean metals sampling and packed with ice to preserve sample integrity. After compositing, samples were shipped for next morning delivery to Pacific EcoRisk.

3.3 SAMPLE COLLECTION FOR DOWNSTREAM SITES DURING DRY WEATHER

In the July 12, 2004 draft Work Plan, there were no sampling sites in the lower reach of the L.A. River; however, SC comments suggested a need to examine the WER in lower freshwater portions of the L.A. River. As such, WER samples were collected from two lower-reach sites at Rosecrans Avenue (LARR) and Willow Street (LARW) downstream of the confluence of the L.A. River and the Rio Hondo and Compton Creek, respectively. For each dry-conditions sampling events [3 summer, 1 winter], samples were collected as manual flow-weighted composites over a 24-hour period. Samples were collected as 2.5 or 3-gallon grab samples every six hours for a 24-hour period. Samples were then mixed together based on flow proportioned volumes to form a composite sample. The amount of water used from each of grab sample was based on the flow rate at the time each sample was collected, similar to the POTW composites. After compositing, samples were shipped for next morning delivery to Pacific EcoRisk.

[4] The 6/29/98 NPDES permit for the BWRP [RWQCB Order No. 98-052] identifies two effluent discharge points to the Burbank Western Wash. Discharge 002 is tertiary effluent discharged directly from the WRP which is adjacent to the Wash. Discharge 001 is discharged to the Wash downstream of discharge point 002 and consists of BWRP effluent mixed with power plant cooling tower blowdown. The City of Burbank has eliminated discharge 001, and therefore only discharge point 002 was considered for the purposes of this study.

3.4 SAMPLE COLLECTION FOR WET WEATHER EVENT

Samples for wet weather WER testing event [during storm flow conditions] were collected from the Los Feliz Bridge (W1) approximately one mile below the LAGWRP, and at the LARR and LARW stations. These sites were selected to provide composite samples comprising of effluent from all three POTWs with a high proportion of storm flow and to represent downstream conditions during the wet season. The wet season wet weather event samples consisted of multiple grab samples collected every four hours for 12 hours during a targeted storm event and combined into a single composite sample for each station. The amount of water used from each of grab sample was based on the flow rate at the time each sample was collected estimated using flow gages in proximity to the sampling stations. The targeted storm event for wet weather sampling was selected based on a reasonable probability that the event would result in substantially increased flows in the L.A. River for at least 12 hours. Appendix D of the Final Work Plan (included as Appendix 2 of this report) presents the protocol used for initiating wet weather sampling event. After compositing, samples were shipped for overnight delivery to Pacific EcoRisk.

3.5 SITE WATER COLLECTION TECHNIQUES

As described previously, site water is generally used to describe receiving water, effluent, or simulated downstream water. All dry weather receiving water samples from LARR, LARW, and R4 (for simulated downstream water) were collected as grab samples by wading into the L.A. River. In general, samples were taken at approximately mid-stream, mid-depth at the location of greatest flow (where feasible). Wet weather receiving water samples at W1, LARR, and LARW were collected as grab samples by lowering a weighted bucket containing a clean sample container (3-gallon jug) into the L.A. River.

Briefly, the key aspects of quality control incorporated into the Final Work Plan are as follows:

1. Field personnel were thoroughly trained in proper use of sample collection equipment and were able to distinguish acceptable versus unacceptable water samples.
2. Field personnel were thoroughly trained to recognize and avoid potential sources of sample contamination (*e.g.*, engine exhaust, ice used for cooling).
3. Sample containers used were the recommended type and cleaned to be free of contaminants (*i.e.*, pre-cleaned).
4. Conditions for sample collection, sample preservation, and holding times were followed.

Sampling events proceeded in the following manner:

1. Before leaving the base of operations, the number and type of sample bottles were confirmed.
2. Upon arrival at a sampling station, general information was noted on a field log sheet.
3. Samples were collected as indicated on the event summary sheet in the manner described in the Final Work Plan. Additional volume and blank samples for field-initiated QA/QC samples were collected as necessary. Sample containers were placed in coolers and carefully packed in ice.
4. Routine water quality characteristics (temperature, pH, DO, and salinity) for each event were measured in the field and recorded on the field log sheet.

Clean sampling techniques were used for all field work (USEPA 1995a). Briefly, grab samples were collected using the following procedures:

1. Clean powder-free nitrile gloves were used when handling bottles and lids. Gloves were changed if the potential for cross-contamination occurred from handling sampling materials or samples;

2. Sample lids were removed and the bottles and caps were rinsed three times before collecting the sample, except if there was sample preservative in the bottle; and,
3. The sample was then placed on ice.

Clean techniques outlined in USEPA Method 1669 (1995a) were used throughout all phases of the sampling and laboratory analytical work, including equipment preparation, water collection, sample handling and storage, and testing. Upon arrival at the laboratory, general water quality of the raw water was measured. Measurements included temperature, pH, and electric conductivity. These initial measurements are presented in Appendix 5. Samples were stored at 4 ± 2°C. Site water samples were used in the toxicity tests within 24-36 hours of collection.

All tubing and sample containers used for the collection of ambient water samples were cleaned following USEPA guidelines (*i.e.*, Alconox®, organic solvent, acid and de-ionized water). Methanol was used as the organic solvent and its use was followed by a minimum of four DI rinses. Methanol was used on field sampling tubing and containers and all laboratory glassware and plastic-ware used in the field.

3.6 DEVIATIONS FROM WORK PLAN SAMPLING PROCEDURES

Due to conditions in the field and actions taken by the field crews, two deviations from the Final Work Plan occurred. During Event 2, conducted on September 19th and 20th 2005, rainfall occurred in the morning hours (after approximately 7 AM) resulting in a visible increase in flow in the L.A. River. The fifth and final receiving water samples were not collected at R4, LARR, and LARW because of increased flow. A review of rainfall, L.A. River flow, and electrical conductivity data taken with field meters at the L.A. River sites indicated that the first four receiving water samples were unaffected by the rain event. Appendix 6 presents the data analysis and discussion of options for conducting laboratory analysis. These options were discussed via conference call with the TAC on September 20th before initiation of sample compositing. The TAC agreed with the analysis and decision to composite the first four receiving water samples. Additionally, the TAC agreed that the event was representative of dry weather conditions even though samples were only collected for an 18-hour period and that the deviation was not expected to affect toxicity and chemical analyses results.

The second deviation from the Final Work Plan occurred during Event 3, conducted between October 5th and 7th. A flow-proportional field compositing error by the LWA sampling crew involving composite bottles from the DCTWRP (Site T1) and BWRP (Site B1) autosamplers on the afternoon of October 6th prevented these two 100% effluent manual composites from being created. This required that another 24-hour composite sampling period be initiated for these two discharge sites (100% effluent) starting in the evening of October 6th and concluding in the evening of October 7th. The composite samples for the other three Event 3 sampling sites (LAG, LARR, and LARW) were not impacted by the compositing error, and were prepared and delivered overnight to Pacific EcoRisk per the Final Work Plan. Because this deviation related only to 100% effluent samples from the two upstream WRPs operating under normal conditions during the Wednesday morning through Friday evening timeframe, the results were representative of the target sampling conditions identified in the Final Work Plan. A review of conventional water quality parameters for T1 and B1 for Event 3 showed no deviation from the effluent quality from Events 1 and 2. Therefore the deviation from the Final Work Plan sampling protocols did not affect toxicity and chemical analyses results.

4 TOXICITY LABORATORY PROCEDURES

4.1 TOXICITY METHODS

All methods for holding and processing toxicity samples as well as conducting toxicity testing conformed to the following guidance for development of a WER:

- Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. Fifth Edition. USEPA 2002. EPA/821/R-02/012.
- Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals. USEPA.1994. EPA/823/B-94/001.
- Streamlined Water-Effect Ratio Procedure for Discharges of Copper. USEPA. 2001. EPA/822/R-01/005.

4.2 LABORATORY WATER AND DILUTION WATER PREPARATION

The "Laboratory Water" tests were performed in water that consisted of USEPA synthetic water (prepared by the addition of reagent grade chemicals [calcium sulfate, magnesium sulfate, sodium bicarbonate, and potassium chloride], in specified proportions to reverse-osmosis, de-ionized water), at a hardness similar to ambient L.A. River water. The use of reconstituted water as a "laboratory water" is consistent with guidance found in EPA-821-R-02-012, EPA-822-R-01-005, and EPA-823-B-94-001. Dilution water used in laboratory water and reference toxicant tests was prepared prior to test initiation. The dilution water consisted of USEPA synthetic freshwater at a hardness within the hardness range of the L.A. River water samples for the event. Hardness was not matched specifically for each sample. Per the Streamlined Procedure, laboratory water with hardness "relatively close" to that of the site water should be used. No further guidance is given as to what relatively close means. The guidance also states that lab waters should be between 40 and 220 mg/L CaCO3. As site waters were often near or above 220 mg/L the lab waters were chosen to be no higher than the upper bound as presented in the WER guidance (i.e., 220 mg/L) and to be as representative as possible for all samples tested. Please note that the lab water results were not used to calculate the final WERs. The laboratory dilution water for reference tests consisted of a mixture of commercial spring waters (80% Arrowhead: 20% Evian).

4.3 RANGE-FINDING TOXICITY TESTS

Range-finding toxicity tests were performed to assure that an appropriate range of copper concentrations were used in definitive testing. The range-finding tests consisted of acute (48-hour) exposures to test solutions prepared by spiking 500-mL aliquots of site water with copper from a certified copper nitrate ($CuNO_3$) solution obtained from Inorganic Ventures of Lakewood, New Jersey. Prior to analyses, test solutions were allowed to sit for approximately three hours consistent with WER guidance. Allowing the samples to sit three hours is intended to avoid exposure of the test organisms to ionic copper. Water quality characteristics (pH, DO, and electrical conductivity) were measured for each test solution prior to use in tests. Table 4 presents the nominal total copper concentrations used in range-finding tests.

Table 4. Nominal Total Copper Concentrations Used In Range-Finding Tests for L.A. River Copper WER

Event	Range-Finding Test Concentrations (Total Cu ug/L)
1	1.0, 10, 50, 100, 250, 500, and 1000
2	50, 100, 200, 500, and 1,000
3	50, 100, 200, 500, and 1,000
4[1]	10, 50, 100, 200, 300, 400, 500, 1000, 1500 and 2,000
5	10, 50, 100, 200, 300, 400, 500, 1000, 1500 and 2,000

1 Event 4 was a wet weather storm event.

Each range-finding test treatment had two replicates, which each consisted of 60-mL test solution in a 100-mL HDPE beaker; a third "water quality" replicate was similarly established for measurement of test solution water quality characteristics. Neonate *C. dubia* (<24 hrs old), from in-house laboratory cultures, were used to start these acute toxicity tests, which were initiated by allocating five *C. dubia* into each replicate cup (USEPA 1993). The test organisms were randomly allocated into each test chamber (*i.e.*, test treatment containers were randomly loaded). The culture media used for rearing the C. dubia is the same media used for the reference toxicant test and is described in section 4.2 (a mixture of commercial spring waters: 80% Arrowhead and 20% Evian). The combination of spring waters results in water that ranges in hardness from 80-100 mg/L as $CaCO_3$ (moderately-hard water as per EPA guidance). The cups containing the test treatments were placed in a temperature-controlled water bath maintained at 20°C, under fluorescent lighting on a 16L:8D photoperiod. Water quality characteristics (pH, DO, and electrical conductivity) for the test waters were measured each day and at the end of the test in the water quality replicate. After 48 hours, the tests were terminated and the number of live neonates in each replicate cup was counted.

Survival data for each site water treatment was analyzed to determine key concentration-response endpoints (*e.g.*, EC50 values). All statistical analyses were performed using the CETIS® statistical package. Results from the range-finding tests were used to determine the nominal definitive test copper concentrations based upon identification of copper concentrations that would be expected to bracket the potential range of *C. dubia* acute toxicity survival EC50 values.

4.4 COPPER SPIKING

Nominal test copper concentrations were selected based on range-finding tests to bracket the expected potential range of EC50 values and attain partial effects results for *C. dubia* survival. Test concentrations were prepared by spiking 500-mL aliquots of laboratory and site waters with a certified $CuNO_3$ standard obtained from Inorganic Ventures of Lakewood, New Jersey. However, the toxicity testing laboratory's historical reference toxicant database was (and continues to be) developed using copper sulfate ($CuSO_4$). The protocol for reference toxicant test performed as part of this Study was maintained for consistency purposes. The use of $CuNO_3$ and $CuSO_4$ are approved for the application for which they were applied.

New "working" stock solutions were prepared for each site and laboratory water for each test event. Stock solutions were prepared by adding copper from an unacidified, certified 1 mg/L copper (as $CuNO_3$) solution to site or laboratory water. The volume of $CuNO_3$ solution added to the "working stock" or highest test concentration, ranged from 0.06-0.6 mL/L . This "working" stock solution was used for preparation (or spiking) of individual test treatments via a serial dilution approach (*i.e.*, a large volume of water was spiked with copper to prepare test solution at the highest nominal copper concentration; an aliquot of that spiked water was then mixed [or diluted] with an aliquot of unspiked water to prepare test solution at the next lower copper concentration; an aliquot of this second copper-spiked test solution was then similarly mixed with an aliquot of unspiked water to prepare the next lower test solution; this process was repeated to prepare each of the copper concentration test solutions for each tested waters). The water volume comprising each test treatment solution was then split between analytical chemistry sample bottles and replicate test chambers to minimize inter-replicate variability with respect to copper concentration.

Prior to analysis, test solutions were allowed to sit for approximately three hours consistent with WER guidance. Allowing the samples to sit approximately three hours is intended to avoid exposure of the test organisms to ionic copper. Table 5 through Table 10 present nominal (*i.e.*, calculated) test copper concentrations used for each event in lab and site water. Each toxicity test had between nine and twelve concentrations of copper. Measured results for toxicity spiking are presented in Appendix 7.

Table 5. Nominal Total Copper Additions to Lab Water for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
Lab Water	1	0, 11.7, 14.7, 18.4, 22.9, 28.7, 35.8, 44.8, 56, 70
Lab Water	2	0, 16.3, 19.2, 22.6, 26.6, 31.3, 36.8, 43.4, 51, 60
Lab Water	3	0, 16.3, 19.2, 22.6, 26.6, 31.3, 36.8, 43.4, 51, 60
Lab Water	4[1]	0, 1, 2, 3, 4.1, 4.8, 5.7, 6.7, 7.8, 9.2, 10.8, 12.8, 15
Lab Water	5	0, 14, 16, 19, 23, 27, 31, 37, 43, 51, 60

1 Event 4 was a wet weather storm event.

Table 6. Nominal Total Copper Additions to DCTWRP (T1) Site Water for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
T1	1	0, 73, 92, 115, 143, 179, 224, 280, 350
T1	2	0, 96, 113, 133, 157, 184, 217, 255, 300
T1	3	0, 96, 113, 133, 157, 184, 217, 255, 300

Table 7. Nominal Total Copper Additions to BWRP (B1) Site Water for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
B1	1	0, 73, 92, 115, 143, 179, 224, 280, 350
B1	2	0, 96, 113, 133, 157, 184, 217, 255, 300
B1	3	0, 96, 113, 133, 157, 184, 217, 255, 300

Table 8. Nominal Total Copper Additions to Simulated Downstream Water (SDW) Comprised of LAGWRP (G1) and Receiving Water (R4) and Los Feliz Ave (W1) for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
SDW[1] (G1 and R4)	1	0, 73, 92, 115, 143, 179, 224, 280, 350
SDW[1] (G1 and R4)	2	0, 96, 113, 133, 157, 184, 217, 255, 300
SDW[1] (G1 and R4)	3	0, 96, 113, 133, 157, 184, 217, 255, 300
W1	4[2]	0, 50, 67.8, 75.3, 83.7, 93, 103, 115, 128, 142, 158, 175
W1	5	0, 105, 116, 129, 143, 159, 177, 197, 219, 243, 270, 300

1 Simulated downstream water (SDW) was created using the 7Q10 approach.
2 Event 4 was a wet weather storm event.

Table 9. Nominal Total Copper Additions to L.A. River at Rosecrans (LARR) Site Water for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
LARR	1	0, 105, 131, 164, 205, 256, 320, 400, 500
LARR	2	0, 160, 189, 222, 261, 307, 361, 425, 500
LARR	3	0, 160, 189, 222, 261, 307, 361, 425, 500
LARR	4[1]	0, 67.8, 75.3, 83.7, 93, 103, 115, 128, 142, 158, 175
LARR	5	0, 105, 116, 129, 143, 159, 177, 197, 219, 243, 270, 300

1 Event 4 was a wet weather storm event.

Table 10. Nominal Total Copper Additions to L.A. River at Willow (LARW) Site Water for L.A. River Copper WER

Site	Event	Nominal Test Concentrations (Total Cu ug/L)
LARW	1	0, 173, 216, 270, 338, 422, 528, 660, 825
LARW	2	0, 264, 310, 365, 430, 505, 595, 700, 823
LARW	3	0, 287, 319, 354, 394, 437, 486, 540, 600
LARW	4[1]	0, 67.8, 75.3, 83.7, 93, 103, 115, 128, 142, 158, 175
LARW	5	0, 105, 116, 129, 143, 159, 177, 197, 219, 243, 270, 300

1 Event 4 was a wet weather storm event.

4.5 TOXICITY TESTING PROCEDURE

The control treatment for site waters consisted of an aliquot of site water without any added copper. Test concentrations were prepared as discussed in section 4.4. Nominal definitive test copper concentrations were selected based on results of the copper range-finding tests performed on site and lab water to bracket the expected range of *C. dubia* acute survival EC50 values. Initial test water quality characteristics (pH, DO, and electrical conductivity) were determined for each treatment test solution prior to use in the tests.

Each test treatment had four replicates, which each consisted of 60-mL test solution in a 100-mL HDPE beaker. An additional "water quality" replicate was established for measurement of test solution water quality characteristics without disturbing test organisms. These acute toxicity tests were initiated by allocating five neonate *C. dubia* (< 24 hrs old), from in-house laboratory cultures, into each of replicate beakers. The test organisms were randomly allocated into each test chamber (*i.e.*, test treatment containers were randomly loaded). Test replicates were then placed in a foam board which floated in a temperature-controlled water bath maintained at 20°C, under fluorescent lighting on a 16L:8D photoperiod.

Water quality characteristics (pH, DO, and electrical conductivity) for a test solution from each treatment were measured in the water quality replicate each day and at the end of the test. After 48 hours, the tests were terminated and the number of live neonates in each replicate cup was counted. Survival data for each test treatment were analyzed and compared to the appropriate control treatment to determine key concentration-response endpoints (*e.g.*, EC50 values). All statistical analyses were performed using the CETIS® statistical package.

A summary of test conditions and acceptability criteria used in *C. dubia* toxicity testing is provided in Appendix 8.

4.6 REFERENCE TOXICANT TESTING

To confirm that *C. dubia* neonates responded to toxic stress in a typical fashion, reference toxicant tests were run concurrently with each site and lab water tests. The lab control/dilution water used for reference toxicant testing consisted of 80% Arrowhead and 20% Evian commercial spring waters. Test solutions were prepared by spiking the reference toxicant test solutions with copper (as $CuSO_4$) at copper concentrations of 4, 8, 16, 32, and 64 ug/L.

Each test treatment had four replicates, which each consisted of 15-mL test solution in a 30-mL plastic cup. The test was initiated by allocating five neonate (< 24 hrs old) *C. dubia*, from in-house laboratory cultures, into each replicate cup. The test organisms were randomly allocated into each test chamber (*i.e.*, test treatment containers were randomly loaded). The replicate cups were placed in a temperature-controlled water bath at 20°C, under cool-white fluorescent lighting on a 16L:8D photoperiod. Water quality characteristics (pH, DO, and electrical conductivity) of the test waters were measured each day and at the end of the test. After 48 hours, the test was terminated and the number of live neonates in each replicate cup was counted. Test results were used to determine EC50 endpoints to compare to the ongoing laboratory reference toxicant database to ensure that test result responses were consistent with previous test results. Statistical analyses were performed using the CETIS® statistical package.

The response endpoints were considered outside of a normal response if the endpoint was outside the typical response range established by PER. The typical response range established by PER is the mean plus or minus 2 standard deviations of the point estimates generated by the 20 most recent previous reference toxicant tests performed by PER. Appendix 7.1 presents a summary of the reference toxicant tests that were performed concurrently with WER testing over the course of the Study. The mean dissolved copper EC50s ranged from 8.6 ug/L to 9.1 ug/L suggesting that there was not a significant change in the sensitivity of the test organisms used throughout the WER testing. PER, at a minimum, performs monthly reference toxicant tests. The data are recorded on a control chart. Appendix 7.2 presents the EC50 control chart representing reference toxicant testing conducted by PER for *C. dubia* over for the time period of the Study (August 2005 to April 2006). Dissolved copper EC50s from standard reference toxicant testing presented in the control charts range from 6.1 ug/L to 12.6 ug/L. The EC50 results for reference toxicant tests performed for this Study were consistent with the laboratory reference toxicant test database presented in the control charts. This indicates that the test organisms used throughout the Study were responding normally to toxic stress.

4.7 COLLECTION OF SITE WATER AND TEST SOLUTIONS

Immediately prior to test initiation and immediately after test termination, water from each treatment was collected from each site and lab water treatments for dissolved copper analysis. Using “clean” techniques, samples were filtered and collected into pre-cleaned 250-mL HDPE bottles supplied by CRG Marine Laboratories. Each bottle was sealed and placed in an insulated cooler and shipped overnight to CRG Marine Laboratories for analysis. Samples were also collected from each unspiked site water test immediately prior to test initiation for additional constituents including those required to use the BLM: DOC, DIC, potassium, magnesium, calcium, sodium, chloride, sulfate, and total sulfide. Theses samples were collected into pre-cleaned bottles supplied by Calscience, placed in an insulated cooler, and shipped overnight to Calscience for analysis.

4.8 MEASUREMENT OF TOXICITY TEST SOLUTIONS FOR COPPER

After toxicity testing was completed, USEPA Interim Guidance and Streamlined Procedure guidance was used to select test solutions for chemical analysis. Instead of measuring all test solutions, the Streamlined Procedure recommends measuring test solutions (for initial and final dissolved copper) that are used in determining the EC50 value. These test solutions include (i) all concentrations in which some, but not all, of the test organisms were adversely affected, (ii) the highest concentration that did not adversely affect any test organisms, (iii) the lowest concentration that adversely affected all of the test organisms, and (iv) control solutions. This Study followed the USEPA recommendation of measuring only values used in determining endpoints but with one modification. WER calculations for this Study are based on EC50s calculated using initial copper concentrations as opposed to final or a time-weighted average of initial and final copper concentrations. As outlined in the Work Plan, this was considered a more conservative approach given that a proportionately greater copper recovery is expected in site water than in lab water when measured at the test conclusion based on the copper recovery observed in the City of San Jose WER study for South San Francisco Bay (1998). The effect of using initial copper concentration on the calculation of EC50s and subsequent WERs is discussed in more detail in Section 6.6.

4.9 ADDITIONAL WORK PLAN LABORATORY PROCEDURES

After receiving samples for Events 2 and 3, Pacific EcoRisk noted pH levels in the samples collected at LARR and LARW exceeded the USEPA standard freshwater testing range of 6.0-9.0 and could result in adverse impacts to the test organisms (*C. dubia*). Data regarding pH sensitivity of *C. dubia* can be found in: Belanger, Scott E. and Donald S. Cherry (1990) *Interacting Effects of pH Acclimation, pH, and Heavy Metals on Acute and Chronic Toxicity to Ceriodaphnia dubia*. As a precaution, Pacific EcoRisk conducted WER tests on LARR and LARW samples amended to lower the pH in addition to conducting WER testing on unaltered LARR and LARW samples. The amendment of the samples did not cause the initiation of testing protocols to exceed hold times outlined in USEPA protocols, nor did it change any other laboratory procedures. The amended samples were analyzed so that if the pH levels in the unaltered LARR and LARW control samples adversely affected the test organisms valid WER testing data would be available. However, high pH levels in the unaltered LARR and LARW control samples did not adversely affect the test organisms. As such, WER testing results for the unaltered LARR and LARW met toxicity testing QA/QC requirements and results from the amended samples were not needed. This deviation from laboratory procedures did not have any effect on the outcome of this Study because results from the amended LARR and LARW samples were not used to calculate the WER.

5 QUALITY ASSURANCE/QUALITY CONTROL

QA/QC practices were maintained during all facets of this Study (sampling, testing, chemical analysis). This is evidenced by the high quality, low variability results attained in compliance with the individual lab's QA/QC criteria. QA/QC data are provided in Appendix 9 along with several summary tables presenting performance on field and laboratory duplicates, blanks, and spike recoveries by constituent. Environmental data is provided in Appendix 10. Each laboratory used is DHS-ELAP certified to perform all analyses in conformance with requirements.

5.1 CHEMISTRY QA/QC

Extensive QA/QC requirements were designed into this Study as part of the agreements with the analytical laboratories that performed the physical, chemical, and biological analyses. This QA/QC analysis summarizes the acceptability of data generated during sampling events. Hold times, analytical accuracy and precision, potential contamination, and conformance to data acceptability criteria were reviewed. Questionable raw data, results or missing data were identified and referred back to the originating lab for further investigation and qualification as appropriate.

Analytical chemistry accuracy and precision were monitored throughout sampling events of this Study using blanks, duplicates and spikes. Accuracy was assessed through percent recovery analysis of external reference standards and matrix-spike experiments. Precision of methods was determined through the calculation of relative percent difference (RPD) between matrix duplicate and field duplicate analyses. Control limits for precision and accuracy for these analyses were 20% maximum RPD, and 75% minimum to 125% maximum recovery, respectively. Potential contamination of environmental samples was investigated by collecting and analyzing lab, field, method, filter, and procedure blanks to determine if contamination arose at the various stages of sampling and analysis.

Analytical results, toxicity test results, and QA/QC results from each sampling event were compared with QA/QC parameters. Limited QA/QC evaluation of hardness, magnesium, TOC, and TSS values was performed given that precision of these parameters was less critical to the interpretation of results.

5.1.1 Chemistry Data Quality

5.1.1.1 Hold Times

USEPA analytical hold time guidelines place requirements on sample filtration, preservation, and/or analysis. These guidelines were consistently met in 98.6% of the environmental samples. Four total sulfide samples collected for Event 5 on March 30, 2006 were analyzed outside of the recommended hold time by one day. These samples are qualified (Appendix 10) as "estimated" values, but have no impact on WER calculations.

5.1.1.2 Blank Contamination

The following sample blank QA/QC issues were identified:

- Total and dissolved copper were detected in equipment blanks during three events and dissolved copper copped was detected in a field blank during one event; however, no data were qualified because environmental concentrations greatly exceeded blank results.

- Dissolved inorganic carbon was detected in an equipment blank during Event 3; however, no data were qualified because environmental concentrations greatly exceeded blank results.
- Total hardness as $CaCO_3$ was detected in one equipment blank; however, no data were qualified because environmental concentrations greatly exceeded blank results.
- Sulfate was detected in equipment blanks during four events, in a field blank the one event it was tested for, and in blank water returned unopened to the lab (trip blank) in the two events it was tested for. No environmental sulfate data were qualified because environmental concentrations greatly exceeded blank results.
- Dissolved organic carbon was detected in one method blank during the five events, in equipment blanks during four events, in field blanks in two events, and in blank water returned unopened to the lab in one event. A total of 12 DOC analytical results over four events were qualified because of blank contamination and these data were reported as “nondetect” at the reported environmental concentration. Multiple steps were taken to address DOC contamination in blank samples, including working with the analytical laboratory to address potential contamination occurring in the filtration process. The corrective action seemed to be effective for Event 2, but was not effective for the remaining events.

Table 11 presents the sample blank results identified as causing QA/QC issues as well as the corresponding data qualifications, where appropriate. Blank contamination did not affect subsequent WER analyses and calculations. However, DOC potentially affects use of the BLM since it is an input parameter to the model. Over 700 chemical analyses were conducted on samples and only 13 data points are qualified (< 2%) suggesting that overall data quality is high.

Table 11. Blank Contamination Observed During L.A. Copper WER Sampling Events

Event	Constituent	Equipment Blank	Field Blank	Trip Blank[1]	Method Blank	Lowest Detected Value	Program Qualifier	# of Data Points Qualified
1	Dissolved Organic Carbon (mg/L)	1.3			1	8.6	UL-EB, UL-MB	2
	Dissolved Copper (ug/L)	0.72			< 0.5	8.14	None	0
	Total Copper (ug/L)	1			< 0.5	11	None	0
	Sulfate (mg/L)	1.3			< 1	160	None	0
2	Dissolved Copper (ug/L)		0.2		< 0.5	6.44	None	0
	Sulfate (mg/L)		3		< 1	110	None	0
3	Dissolved Inorganic Carbon (mg/L)	1.3			< 0.5	35	None	0
	Dissolved Organic Carbon (mg/L)	1	0.75		< 0.5	7.9	UL-EB	4
	Dissolved Copper (ug/L)	0.3			< 0.5	8.87	None	0
	Total Copper (ug/L)	0.39			< 0.5	9.19	None	0
	Sulfate (mg/L)	1.4	1.3		< 1	120	None	0
	Total Hardness as CaCO3 (mg/L)		1.3		< 5	180	None	0
4	Dissolved Organic Carbon (mg/L)	5.7	< 0.5	6.3	< 0.5	4.3	UL-EB, UL-TB	3
	Sulfate (mg/L)	1.6	1.4	1.5	< 1	20	None	0
5	Dissolved Organic Carbon (mg/L)	1.6	5.1	< 0.5	< 0.5	10	UL-EB, UL-FB	3
	Sulfate (mg/L)	1.4	1.4	1.3	< 1	200	None	0
	Dissolved Copper (ug/L)	0.78	< 0.5	NA	< 0.5	14.2	None	0
	Total Copper (ug/L)	0.35	< 0.5	NA	< 0.5	14.3	None	0

1 Trip Blank – represented a blank water bottle that was returned to the lab unopened. This was done to determine whether the potential existed for blank water to be contaminated in the laboratory before sending it to the field.
UL-FB – Qualifier indicating upper limit of detection based on detected concentration in the field blank.
UL-MB – Qualifier indicating upper limit of detection based on detected concentration in the method blank.
UL-EB – Qualifier indicating upper limit of detection based on detected concentration in the equipment blank.
UL-TB – Qualifier indicating upper limit of detection based on detected concentration in the trip blank.

5.1.1.3 Precision

The purpose of analyzing duplicates is to demonstrate precision of sample preparation and analytical methods. If the RPD for any analyte in laboratory or field duplicate is greater than 15% or 20% (depending on the constituent) *and* the absolute difference between duplicates is greater than the reporting limit, the analytical process was not performed adequately for the analyte and would be qualified. Laboratory and field duplicate samples were analyzed and did not require any data qualifications.

5.1.1.4 Accuracy

Percent recoveries of external reference standard measurements and matrix-spike duplicates were deemed acceptable when measured values were between 70-130% (depending on the constituent) of certified concentration values. During one event, DOC spike samples were out of the acceptable range and during another event TOC spike samples were out of the acceptable range; however, the associated laboratory control sample and/or laboratory control sample duplicate was within control standards and, therefore, the sample data were not qualified. The purpose of analyzing laboratory control samples (or a standard reference material) is to demonstrate the accuracy of sample preparation and analytical methods. Laboratory control samples were analyzed at the rate of one per sample batch. If recovery of any analyte is outside the acceptable range, the analytical process has not been performed adequately for that analyte.

The associated results do not affect subsequent WER analyses and calculations. However, DOC potentially affects use of the BLM since it is an input parameter to the model (see Appendix 13).

5.2 TOXICITY TEST QA/QC

Test acceptability requirements set forth in the USEPA Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms (USEPA 1995b) and WER test guidance (USEPA 1994) were used to assess toxicity data. A summary of test conditions and acceptability criteria used in *C. dubia* toxicity testing is provided in Appendix 8.

5.2.1 Standard Test Conditions/Test Acceptability Criteria

Toxicity testing of ambient site waters with *C. dubia* incorporated standard QA/QC procedures to ensure that test results were valid, including use of negative controls, positive controls, test replicates, and measurement of water quality during testing. These QA/QC procedures are consistent with methods described in the USEPA guidelines. Water samples for toxicity testing were shipped/stored at ≤4°C and used within the 36-hour hold time to determine if site water caused toxicity. WER toxicity tests were initiated within the 96 hours identified in the Streamlined Procedure. All measurements of water quality characteristics were performed as described in the PER Standard Operating Procedures.

5.2.2 Toxicity Hold Times

Table 12 provides sample collection dates and respective test initiations. All WER toxicity tests were initiated within the 96-hour hold time outlined in the Streamlined Procedure.

Table 12. L.A. Copper WER Study Sample Collection and Toxicity Test Initiation Dates

Event	Site Water Collection Date	Range-finding Toxicity Testing Initiation Date	WER Toxicity Testing Initiation Date
1	8/17/05	8/18/05	8/20/05
2	9/20/05	9/21/05	9/23/05
3	10/6/05	10/7/05	10/9/05
	10/7/05	10/8/05	10/9/05
4	2/28/06	3/1/06	3/3/06
5	3/27/06	3/28/06	3/30/06

5.3 COMPARISON TO STANDARD PARAMETERS

The Interim Guidance suggests that parameters collected during WER sampling events be compared to long-term average and median concentrations of these same parameters. Hardness (as $CaCO_3$), total suspended solids (TSS), total copper, and flow data from the POTWs were compared to available historical records and presented in Table 13 through Table 16. The POTWs do not collect dissolved data as part of their regular monitoring. The comparisons indicate that these parameters are within the expected range for the sites.

Table 17 through Table 23, present comparisons of available historical DO, pH, hardness (as CaCO3), total and dissolved copper, TSS, and flow data collected in L.A. River reaches 1, 2, and 3 to data collected at receiving water sites W1, LARR, and LARW. The availability of historical data for the receiving water stations sampled in this Study is limited in some cases to two years. The comparisons indicate that these parameters are generally within the expected range for the sites.

Table 13. Comparison of Hardness (mg/L as $CaCO_3$) Measured in POTW Effluent and Simulated Downstream Receiving Water Samples to Historical Average Hardness (mg/L as $CaCO_3$)

Site	T1	B1	SDW[1]
Event 1	124	165	238
Event 2	141	170	230
Event 3	185	180	235
Historical Data			
Site	**T1**	**B1**	G1
n	138	37	112
n detected	111	37	112
Historical Mean	172	202	235
Standard Deviation	40.0	24.8	25.8
Lower 95% Confidence Limit about Mean	165	194	230
Upper 95% Confidence Limit about Mean	180	210	240
95th Percentile	231	249	281
Historical Median	169	200	233
Min Detected	125	133	142
Max Detected	418	250	312
Date Range	10/98-12/07	6/03-6/06	9/98-12/07

1 For the purposes of this comparison Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4 was compared to LAG effluent (site G1).

Table 14. Comparison of Total Suspended Solids Measured in POTW Effluent and Simulated Downstream Receiving Water Samples to Historical Average Total Suspended Solids (mg/L)

Site	T1	B1	SDW[1]
Event 1	<0.5	<0.5	6
Event 2	<0.5	<0.5	<0.5
Event 3	<0.5	<0.5	7.3
Historical Data			
Site	**T1**	**B1**	**G1**
n	120	1035	120
n detected	44	741	120
Historical Mean	1.49	1.37	2.44
Standard Deviation	0.64	0.62	1.09
Lower 95% Confidence Limit about Mean	1.37	1.33	2.25
Upper 95% Confidence Limit about Mean	1.60	1.40	2.64
95th Percentile	2.83	2.51	4.98
Historical Median	1.34	1.23	2.18
Min Detected	1.00	1.00	1.00
Max Detected	4.18	4.00	5.17
Date Range	1/98-12/07	1/04-10/06	1/98-12/07

Note: <0.5 represents that TSS was not detected in the sample at a detection limit of 0.5 mg/L
1 For the purposes of this comparison Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4 was compared to LAG effluent (site G1).

Table 15. Comparison of Total Copper Measured in POTW Effluent and Simulated Downstream Receiving Water Samples to Historical Average Total Copper (ug/L)

Site	T1	B1	SDW[1]
Event 1	30.4	65.6	13.2
Event 2	23.3	18.2	9.57
Event 3	24.9	53.8	13.0
Historical Data			
Site	**T1**	**B1**	**G1**
n	138	104	140
n detected	136	104	116
Historical Mean	22.7	26.6	12.0
Standard Deviation	6.58	11.0	4.82
Lower 95% Confidence Limit about Mean	21.6	24.5	11.2
Upper 95% Confidence Limit about Mean	23.8	28.7	12.8
95th Percentile	36.2	52.5	21.4
Historical Median	21.7	24.2	11.1
Min Detected	10.0	6.20	4.00
Max Detected	47.3	64	32.0
Date Range	1/98-12/07	8/03-12/07	1/98-12/07

1 For the purposes of this comparison Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4 was compared to LAG effluent (site G1).

Table 16. Comparison of POTW Effluent Flow Rates to Historical Average Flow (cfs)

Site	T1	B1	G1
Event 1	31.0	9.2	8.6
Event 2	32.4	11.6	9.3
Event 3	31.1	8.1	10.1
Historical Data			
Site	**T1**	**B1**	**G1**
n	814	821	743
n detected	814	821	743
Historical Mean	59	8.1	12.6
Standard Deviation	13.7	2.37	7.34
Lower 95% Confidence Limit about Mean	58.1	7.9	12.1
Upper 95% Confidence Limit about Mean	59.9	8.3	13.2
95th Percentile	83.0	12.3	40.5
Historical Median	57.5	7.8	9.4
Min Detected	26.3	3.5	0.01
Max Detected	114	16.0	65.8
Date Range	1/04-3/06	1/04-3/06	1/04-3/06

Note: Data were not available for all days for all POTWs

Table 17. Comparison of Dissolved Oxygen Measured in Receiving Water Samples to Historical Average Dissolved Oxygen Measured at Comparable Locations (mg/L)

Site	W1[1]			LARR[1, 2]			LARW[1, 2]		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
Event 1	---	---	---	6.20	16.8	10.7	5.24	21.6	13.9
Event 2	---	---	---	4.13	23.1	11.2	3.95	21.4	12.2
Event 3	---	---	---	6.35	21.1	13.5	4.52	22.8	14.9
Event 4	9.12	9.76	9.45	8.86	10.4	9.53	8.50	10.0	9.24
Event 5	5.69	9.32	7.08	6.71	14.5	10.8	5.80	14.9	10.9
Historical Data									
n	14			57			37		
Historical Average	10.9			16.0			9.8		
Historical Median	8.26			15.7			9.5		
Min Detected	6.03			8.44			1.4		
Max Detected	50.2			27.4			19.4		
Date Range	6/03 - 5/04			4/02 - 5/04			12/97 - 8/05		

Note: Historical data collected at sites within the same reach as W1, LARR, and LARW were used to develop summary information presented in this table.
- Dashes indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.
1 Multiple DO measurements were taken during each event.
2 Several DO measurements were significantly higher than an expected range for a river. However, certain sections of the L.A. River have significant amounts of algae and relative high temperatures which can result in relatively high DO levels. The DO levels measured during the L.A. River Cu WER study were within the accuracy range of the field meter used to collect the measurements. The DO returned to near saturation during the WER testing.

Table 18. Comparison of pH Measured in Receiving Water Samples to Historical Average pH Measured at Comparable Locations

Site	W1[1]			LARR[1]			LARW[1]		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
Event 1	---	---	---	7.87	9.35	8.57	8.19	10.3	9.17
Event 2	---	---	---	7.78	9.98	8.86	8.6	10.3	9.39
Event 3	---	---	---	8.08	10.2	9.08	8.52	10.5	9.48
Event 4	7.92	8.16	7.99	7.97	8.13	8.03	7.59	8.11	7.94
Event 5	7.78	8.69	8.14	8.16	9.63	8.73	8.12	10.2	9.07
Historical Data									
n	15			62			58		
Historical Average	7.9			9.47			8.18		
Historical Median	7.8			9.4			8.3		
Min Detected	7.6			7.89			3.1		
Max Detected	8.6			11.5			10.3		
Date Range	5/03 - 5/04			4/02 - 9/05			12/97 - 2/06		

Note: Historical data collected at sites within the same reach as W1, LARR, and LARW were used to develop summary information presented in this table.
– Dash indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.
1 Multiple pH measurements were taken during each event.

Table 19. Comparison of Hardness (mg/L as $CaCO_3$) Measured in Receiving Water Samples to Historical Average Hardness (mg/L as $CaCO_3$) Measured at Comparable Locations

Site	W1	LARR	LARW
Event 1	---	271	256
Event 2	---	282	272
Event 3	---	296	278
Event 4	39.6	46.1	46.3
Event 5	228	248	239
Historical Data			
Site	**W1**	**LARR**	**LARW**
n	192	75	67
n detected	192	75	67
Historical Mean	291	307	210
Standard Deviation	54.6	110	101
Lower 95% Confidence Limit about Mean	283	282	186
Upper 95% Confidence Limit about Mean	299	332	235
95th Percentile	388	475	504
Historical Median	286	290	177
Min Detected	83.3	74.3	41.0
Max Detected	470	745	434
Date Range	11/98-11/07	1/05-11/07	10/00-11/07

Note: Historical data collected at a site within the same reach as W1 were used to develop summary information.
--- Dash indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.

Table 20. Comparison of Total Copper Measured in Receiving Water Samples to Historical Average Total Copper Measured at Comparable Locations (ug/L)

Site	W1	LARR	LARW
Event 1	---	13.1	11
Event 2	---	11.5	11.7
Event 3	---	9.73	9.19
Event 4	19.0	25.9	22.5
Event 5	14.3	46.3	38.2
Historical Data			
Site	**W1**	**LARR**	**LARW**
n	329	162	108
n detected	266	135	95
Historical Mean	15.2	15.4	17.6
Standard Deviation	7.75	9.21	28.7
Lower 95% Confidence Limit about Mean	14.4	13.9	12.20
Upper 95% Confidence Limit about Mean	16.1	16.8	23.03
95th Percentile	28.9	30.0	31.7
Historical Median	13.7	13.6	13.7
Min Detected	5.3	5.6	5.1
Max Detected	78.4	72	295
Date Range	2/98-12/07	1/01-10/07	10/00-10/07

Note: Historical data collected at a site within the same reach as W1 were used to develop summary information.
--- Dash indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.

Table 21. Comparison of Dissolved Copper Measured in Receiving Water Samples to Historical Average Dissolved Copper Measured at Comparable Locations (ug/L)

Site	W1	LARR	LARW
Event 1	---	8.14	9.09
Event 2	---	7.09	6.44
Event 3	---	8.87	12.9
Event 4	2.63	3.13	3.59
Event 5	14.2	38.7	33.9
Historical Data			
Site	**W1**	**LARR**	**LARW**
n	174	160	106
n detected	123	103	76
Historical Mean	12.2	11.5	9.83
Standard Deviation	5.22	4.38	3.76
Lower 95% Confidence Limit about Mean	11.4	10.8	9.11
Upper 95% Confidence Limit about Mean	12.9	12.1	10.5
95th Percentile	21.9	19.9	17.6
Historical Median	11.2	10.7	9.12
Min Detected	5.3	4.7	3.61
Max Detected	43.7	26	23.1
Date Range	1/01-10/07	1/01-10/07	10/00-10/07

Note: Historical data collected at a site within the same reach as W1 were used to develop summary information.
--- Dash indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.

Table 22. Comparison of Total Suspended Solids Measured in Receiving Water Samples to Historical Average Total Suspended Solids Measured at Comparable Locations (mg/L)

Site	W1	LARR	LARW
Event 1	---	27	16
Event 2	---	26	44.2
Event 3	---	11.3	15
Event 4	224	200	183
Event 5	8.0	9.3	10.5
Historical Data			
Site	**W1**	**LARR**	**LARW**
n	329	55	42
n detected	329	55	42
Historical Mean	17.4	35.2	151
Standard Deviation	22.3	42.3	286
Lower 95% Confidence Limit about Mean	15.0	24.0	64.4
Upper 95% Confidence Limit about Mean	19.9	46.4	237
95th Percentile	29.5	85.0	511
Historical Median	15.1	23.2	57.8
Min Detected	5	8	6
Max Detected	378	162	1339
Date Range	3/06-12/07	9/00-12/07	9/00-12/07

Note: Historical data collected at a site within the same reach as W1 were used to develop summary information.
--- Dash indicates the parameter was not measured as samples were not collected at site W1 during Events 1 through 3.

Table 23. Comparison of Flow Rates Measured at Receiving Water Sites to Historical Average Flow Rates Measured at Comparable Locations (cfs)

Site	W1[1]	LARR[2]	LARW[3]
Event 1	---	105	134
Event 2	---	118	134
Event 3	---	97	144
Event 4	4,468	10,335	14,071
Event 5	138	155	186
Historical Data			
Site	**W1[1]**	**LARR[2]**	**LARW[3]**
n	788	793	787
n detected	788	793	787
Historical Mean	682	774	1306
Standard Deviation	3098	3218	4542
Lower 95% Confidence Limit about Mean	466	550	988
Upper 95% Confidence Limit about Mean	898	998	1623
95th Percentile	1109	802	2115
Historical Median	159	131	343
Min Detected	36	39	123
Max Detected	73,013	33,789	55,025
Date Range	1/04-3/06	1/04-3/06	1/04-3/06

--- Dashed line indicates flow measurements were not collected at this site during the event.
Note that data points used to calculate average and median values were not separated into wet and dry data.
1 Event 4 flows were obtained from the flow gage located at Tujunga Boulevard eight miles upstream of W1. Event 5 flows were measured in the river by field staff.
2 Event 1, 2, 3, and 5 flows were measured in the river by field staff. Event 4 flows were obtained from the flow gage located at Firestone Boulevard approximately three miles upstream of LARR.
3 LARW flows were obtained from the flow gage located at Wardlow Road approximately one mile upstream of LARW.

5.4 QA/QC CONCLUSIONS

All results are complete with sufficient quality assurance data to support the validity of the reported chemical and toxicological data required to develop a copper WER. The QA/QC issues discussed above do not affect the WER calculations.

6 RESULTS

The following section presents analytical results to evaluate variability in composite samples and the assumptions of water quality during “shoulder events”. Additionally, chemistry and toxicity results are presented, as well as the calculation of sample WERs (sWERs), and a statistical analysis of variations in sWERs based on season, weather condition, and location within the L.A. River. Appendix 10 presents the environmental data collected for this Study and is referenced throughout this section. Toxicity spiking results are presented in Appendix 7.

6.1 VARIABILITY ANALYSIS

On July 20, 2005 water samples were collected for a composite sample variability analysis (a.k.a. degradation analysis), as requested by the TAC. Concern was expressed by the TAC that collection of samples as 24-hour composites could lead to variability in chemical parameters that affect the bioavailability of copper and could subsequently affect the resulting WER toxicity tests. Chemical parameters measured as part of this assessment included parameters likely to affect the bioavailability of copper (dissolved organic carbon and hardness as CaCO3), general parameters (specific conductance, pH, dissolved oxygen), and total and dissolved copper. Use of 24-hour composite samples is a generally accepted method for representing chemical parameters over a 24-hour period and is intended to provide a representative sample of influent, effluent or receiving waters. It was not the purpose or intent of this variability analysis to be a definitive study on variability of chemical concentrations in 24-hour composites. Rather, the purpose of the variability analysis was to conduct a single event to confirm that the generally accepted method of 24-hour composite sample collection was appropriate for this study. The variability analysis sample was collected as a grab sample into multiple sample bottles in the L.A. River at R4 (Figure 2). The sample bottles were placed on ice in separate ice chests and shipped to two laboratories. CRG analyzed total and dissolved copper and Calscience analyzed DOC, hardness, pH, electrical conductivity, and DO. The laboratories were instructed to analyze a portion of the sample upon receipt and report the results as T=0 (time equals “zero”) and to re-analyze the sample 24 hours after sample receipt and report the results as T=24 (time equals 24 hours).

Table 24 presents the variability analysis results. The results of the variability analysis do not indicate a significant difference between samples analyzed immediately upon receipt or 24 hours after receipt, except for DO. This suggests that using composite samples for this Study will appropriately represent in-stream conditions and result in a representative WER.

Table 24. Analytical Results for L.A. River Copper WER Variability Analysis

Constituent/Parameter	T=0	T=24	Percent Difference
Dissolved Organic Carbon	11 mg/L	11 mg/L	0%
Total Hardness (as $CaCO_3$)	320 mg/L	330 mg/L	3%
Specific Conductance	1100 umhos	1100 umhos	0%
pH	8.28 pH units	8.44 pH units	1.9%
Dissolved Oxygen	11.4 mg/L	9.43 mg/L	21%
Total Copper	9.04 ug/L	9.57 ug/L	5.5%
Dissolved Copper	6.22 ug/L	6.21 ug/L	0.2%

6.2 ANALYSIS OF "SHOULDER EVENT" DATA

A memorandum was prepared (Appendix 11) to provide an analysis used to define a "shoulder event" based on flow conditions as well as the results of mass balance-based simulations performed to address the possible effects of a wet weather "shoulder event" on copper effluent limits. The "shoulder event" condition has been identified as elevated base flows resulting from dam releases following storm events. A "shoulder event" is defined as a period of at least 5 consecutive days in which the flow rate is within the 75th and 90th percentiles of flows measured at the Firestone Blvd gauging station (178 cfs and 414 cfs, respectively). Concern was expressed by the stakeholder group that "shoulder event" conditions could represent the critical condition for copper bioavailability in the L.A. River. The overall purpose of this analysis was to determine the most likely critical flow conditions, based on realistic flow and water quality scenarios. Critical flow conditions were defined as those flows that resulted in the lowest assimilative capacity and copper effluent limits for the DCTWRP. The "shoulder event" condition was identified as elevated base flows resulting from dam releases following storm events and defined as a period of at least five consecutive days in which the flow rate is within the 75th (*e.g.*, 178 cubic feet per second [cfs]) and 90th (*e.g.*, 414 cfs) percentiles of flows measured at the Firestone Blvd. gaging station. Flows meeting this criterion occurred in 52% of the years from 1985 to 2005. Mass balance simulations were performed for a range of flow and water quality scenarios for the DCTWRP. The methods and detailed results of these simulations are presented in Appendix 11. Although critical flow conditions were defined based on the DCTWRP, shoulder events are believed to have occurred, at least in part, due to releases from two dams in the Tujunga Creek watershed (Big Tujunga and Hansen Dams). Additionally, DCTWRP effluent assimilates downstream discharges from the Tujunga Wash. As such, to solidify the resolution of this issue, DOC and copper samples were collected from the Hansen Dam reservoir discharge after one storm to determine if the reservoir water quality conditions identified in the shoulder analysis could be problematic.

The simulation results clearly indicate that dry weather base flows represent the critical sampling condition for this Study. Based on these results, it was not necessary to target wet weather or wet season "shoulder event" conditions for WER toxicity testing. However, to address any lingering doubts as to whether more unrealistic "shoulder event" conditions actually occur, a sample was collected from the Hansen Dam spillway which contains water from contributing drainages that are in part responsible for the elevated wet season base flows downstream of DCTWRP. The sample was collected between wet weather events and, per the August 14, 2005 memo (Appendix 11), analyzed for DOC and dissolved copper. Table 25 presents the analytical results of the "shoulder event" sample. The results match the assumptions presented in the memo, in that water quality had relatively low copper concentrations (compared to urban drainages) and moderate DOC concentrations, which equate to moderate WERs. Consequently, "shoulder event" conditions do not represent a critical condition. It is most likely upstream that water quality conditions during the "shoulder event" would result in low to average WERs and low to average dissolved copper concentrations.

Table 25. Analytical Results from L.A. River Copper WER "Shoulder Event" Sampling at the Hansen Dam Spillway on April 5, 2006

Constituent	Concentration	Units
Dissolved Organic Carbon	6.7	mg/L
Dissolved Copper	2.2	ug/L

6.3 CHEMISTRY SUMMARY STATISTICS

Table 26 through Table 29 present summary statistics for dissolved copper, hardness, DOC, and TSS data measured in ambient samples. Figure 3 presents a comparison of total and dissolved copper data analyzed in samples collected at each sample site. It was noted that there is significant variability in copper concentrations in the BWRP effluent and at LARR and LARW during Event 5. It is not clear why copper concentrations were higher in Event 5; however, the additional copper loading could be due to discharges from upstream tributaries and/or urban runoff. Regardless, the elevated copper concentrations do not affect the WER calculations. Figure 4 presents a comparison of total and dissolved copper data based on samples collected during wet and dry weather. Figure 4 indicates dissolved copper makes up a lower proportion of copper in wet weather samples than in dry weather samples. Dissolved copper comprised between 55 to 100% of total copper in dry weather samples and between 12 and 16% of total copper in wet weather samples (Event 4). Note the wet event, Event 4, had significantly higher TSS (Table 29) than the dry events. In two instances, measured dissolved copper values were greater than total copper values. Data were not available for toxicity spiking because only dissolved copper was analyzed in these samples.

Table 26. Dissolved Copper Ambient Concentrations (ug/L) Measured During L.A. River Copper WER Sampling

Event #	T1	B1	SDW[1]	W1	LARR	LARW
1	28.6	65.5	11.5	---	8.14	9.09
2	22.1	17.4	8.68	---	7.09	6.44
3	24.7	55.9	11.5	---	8.87	12.9
4	---	---	---	2.63	3.13	3.59
5	---	---	---	14.2	38.7	33.9
arithmetic mean	25.1	46.3	10.6	8.4	13.2	13.2

1 Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4.
Dashes indicate the parameter was not measured as samples were not collected at the site during the event.

Table 27. Total Hardness as $CaCO_3$ Ambient Concentrations (mg/L) Measured During L.A. River Copper WER Sampling

Event #	T1	B1	SDW[1]	W1	LARR	LARW
1	124	165	238	---	271	256
2	141	170	230	---	282	272
3	185	180	235	---	296	278
4	---	---	---	39.6	46.1	46.3
5	---	---	---	228	248	239
arithmetic mean	150	172	234	134	229	218

1 Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4.
Dashes indicate the parameter was not measured as samples were not collected at the site during the event.

Table 28. Dissolved Organic Carbon Ambient Concentrations (mg/L) Measured During L.A. River Copper WER Sampling

Event #	T1	B1	SDW[1]	W1	LARR	LARW
1	12	8.6	11	---	15	17
2	11	7.8	8.8	---	11	10
3	12	7.9	9.3	---	8.7	9.9
4	---	---	---	4.3	5	7.2
5	---	---	---	10	10	10
arithmetic mean	11.7	8.1	9.7	7.2	9.9	10.8

1 Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4.
Dashes indicate the parameter was not measured as samples were not collected at the site during the event.

Table 29. Total Suspended Solids Ambient Concentrations (mg/L) Measured During L.A. River Copper WER Sampling

Event #	T1	B1	SDW[1]	W1	LARR	LARW
1	<0.5	<0.5	6	---	27	16
2	<0.5	<0.5	<0.5	---	26	44.2
3	<0.5	<0.5	7.3	---	11.3	15
4	---	---	---	224	200	183
5	---	---	---	8	9.3	10.5
arithmetic mean	NC	NC	6.7	116	54.7	53.7

1 Simulated Downstream Water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4.
Dashes indicate the parameter was not measured as samples were not collected at the site during the event.
NC Not calculated because there are insufficient data.

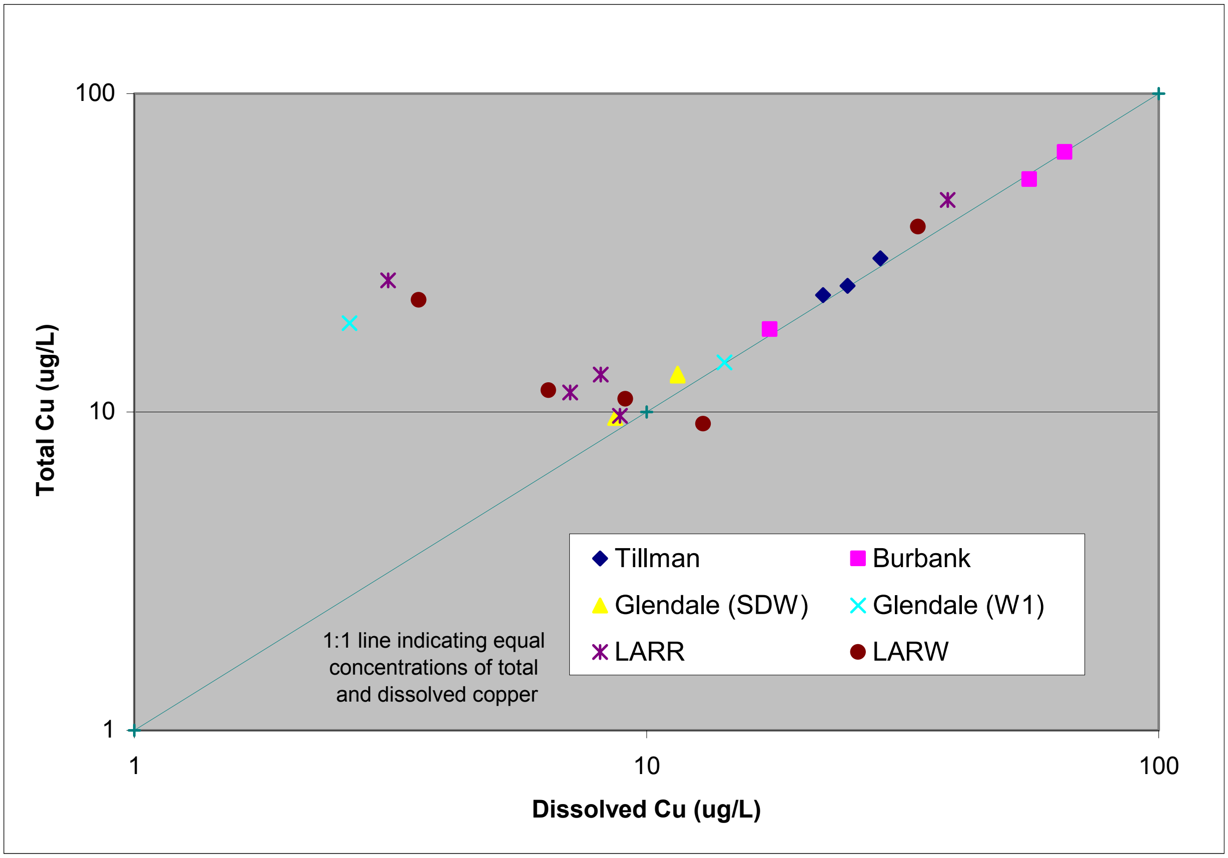

Figure 3. Dissolved Versus Total Copper Concentrations Measured in Site Water for the L.A. River Copper WER Study by Site

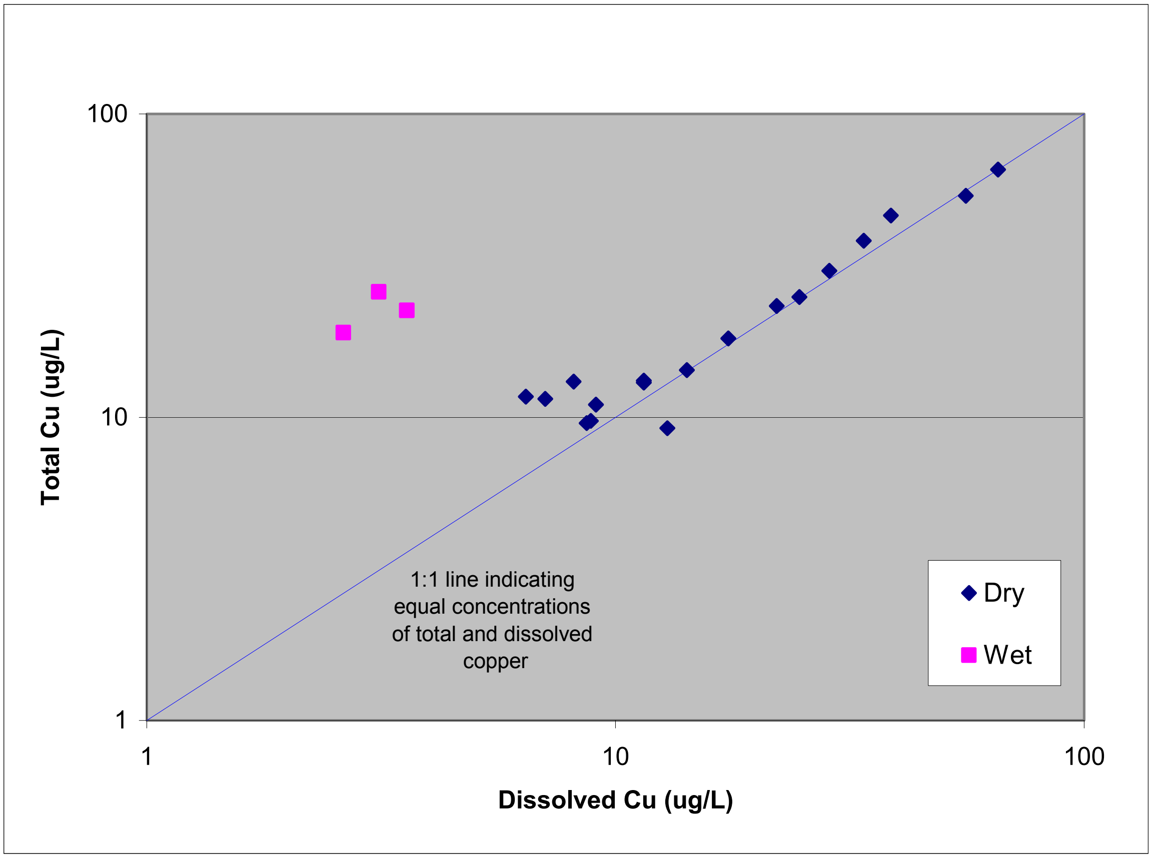

Figure 4. Dissolved Versus Total Copper Concentrations Measured in Site Water for the L.A. River Copper WER Study by Wet and Dry Weather

6.4 TOXICITY TESTING RESULTS

Concentration-response plots for each site and lab water toxicity tests are presented in Figure 5 through Figure 10. Figure 11 presents concentration-response plots for all sites and lab water. Data collected from the SDW comprised of effluent (G1) and receiving water (R4) are considered in Figure 8 and the remaining analysis with Glendale site W1 because these sites are located in the same reach of the L.A. River. The concentration-response plots were normalized to a standard hardness of 200 mg/L as $CaCO_3$ to allow comparison of results across events. The methodology used for normalizing hardness is presented below (USEPA 2001):

$$EC50_{\text{at Standard Hardness}} = EC50_{\text{at Sample Hardness}} \times \left(\frac{\text{Standard Hardness}}{\text{Sample Hardness}} \right)^{0.9422}$$

The "% Survival" on the y-axis represents the percentage of test organisms that were not adversely affected at a specific copper concentration. All curves show expected effects of the organisms being exposed to increasing copper concentrations. Table 30 presents dissolved copper EC50 results for site and lab water for Events 1 through 5. Figure 12 presents dissolved copper EC50 results normalized to a standard hardness of 200 mg/L as $CaCO_3$ for site and lab water for Events 1 through 5. EC50 results are normalized to a standard hardness throughout the report to allow for a comparison of EC50s between sites and events. The choice of a standard hardness of 200 mg/L as $CaCO_3$ is arbitrary and does not affect the calculation of WER values. Toxicity spiking results are presented in Appendix 7.

EC50 values were determined following the protocols set forth in USEPA's 2002 Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition. Statistical analysis was performed using CETIS software based on the Automated Decision Tree presented in USEPA 2002. CETIS allows the selection of the regression analysis to be performed. Per the decision tree, Probit analysis was initially performed in all cases and if the data did not conform to the assumptions of the Probit method (i.e. two or more partial responses) CETIS would provide an error message indicating that "two or more partial responses" are required; in these cases (per the decision tree) the Spearman-Karber Method was used.

The Spearman-Karber method contained in the CETIS software is based on the USEPA's Trimmed Spearman-Karber v1.5 Application and is used in the recommended "Automatically Minimize Trim Level" option. In this option, data that does not meet the assumption of the Probit method, but which does meet the assumption of the Spearman-Karber Method, is evaluated by following the assumptions required for the Spearman-Karber Method (complete mortality at one of the treatment concentrations and no partial responses [0% trim] and 100% survival in the lowest treatment concentration). If the assumptions for use of the Spearman-Karber Method are not met, the CETIS program automatically applies the minimum trim level needed and performs the analysis conforming to the Trimmed Spearman-Karber Method; all print outs indicate that the Trimmed Spearman-Karber was performed regardless of whether the Spearman-Karber Method or Trimmed Spearman-Karber analyses was applied.

Per the Work Plan (LWA 2005), range-finding tests were used to select copper concentrations for definitive tests. Given the requirement for an additional 48-hour holding of the samples, some concern existed that copper binding capacity of site waters was potentially altered. To address this concern plots were generated comparing hardness-normalized nominal copper concentrations for both range-finding and definitive toxicity tests against percentage effect. The comparison allows for an evaluation of whether the concentration response was similar in the range-finding and definitive toxicity tests for each sample. These plots, as well as a table presenting the results are included in Appendix 12 and indicate that the additional 48-hour hold time did not affect copper toxicity of the effluents or site waters.

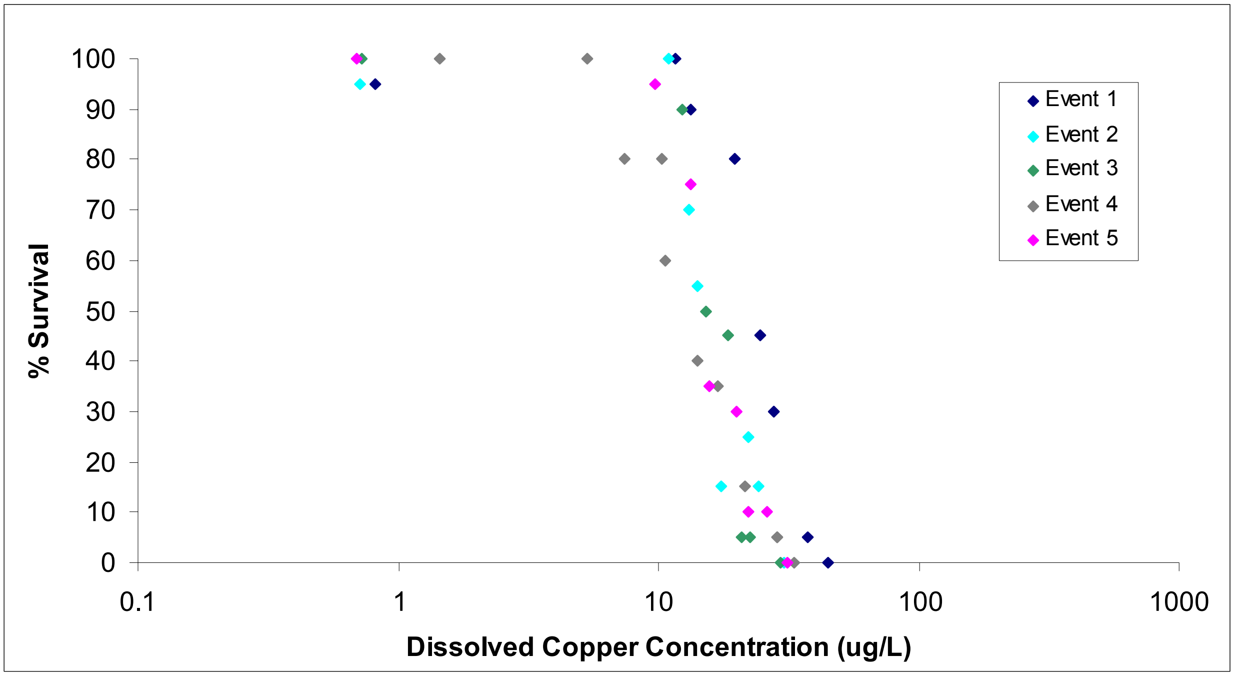

Figure 5. Concentration-Response Curves for Lab Water – L.A. River Copper WER Hardness Normalized to 200 mg/L (as CaCO3)

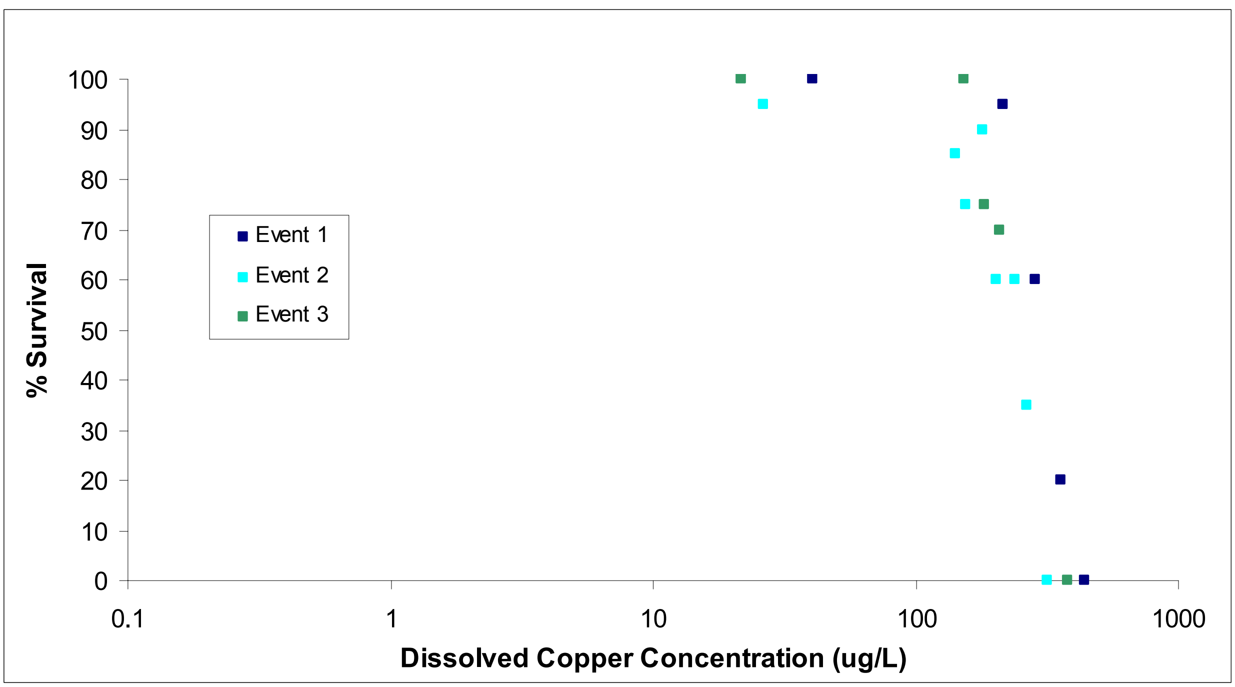

Figure 6. Concentration-Response Curves for Donald C. Tillman WRP Effluent (Site T1) Hardness-normalized to 200 mg/L as $CaCO_3$

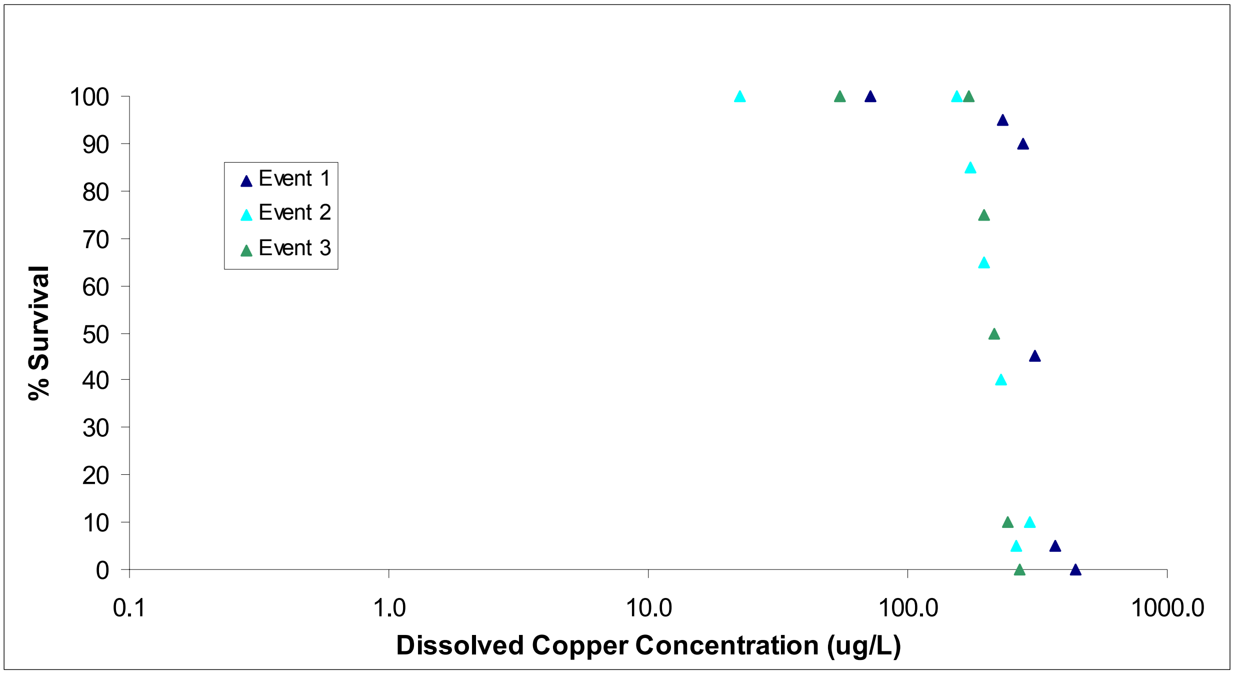

Figure 7. Concentration-Response Curves for Burbank WRP Effluent (Site B1)
Hardness-normalized to 200 mg/L as $CaCO_3$

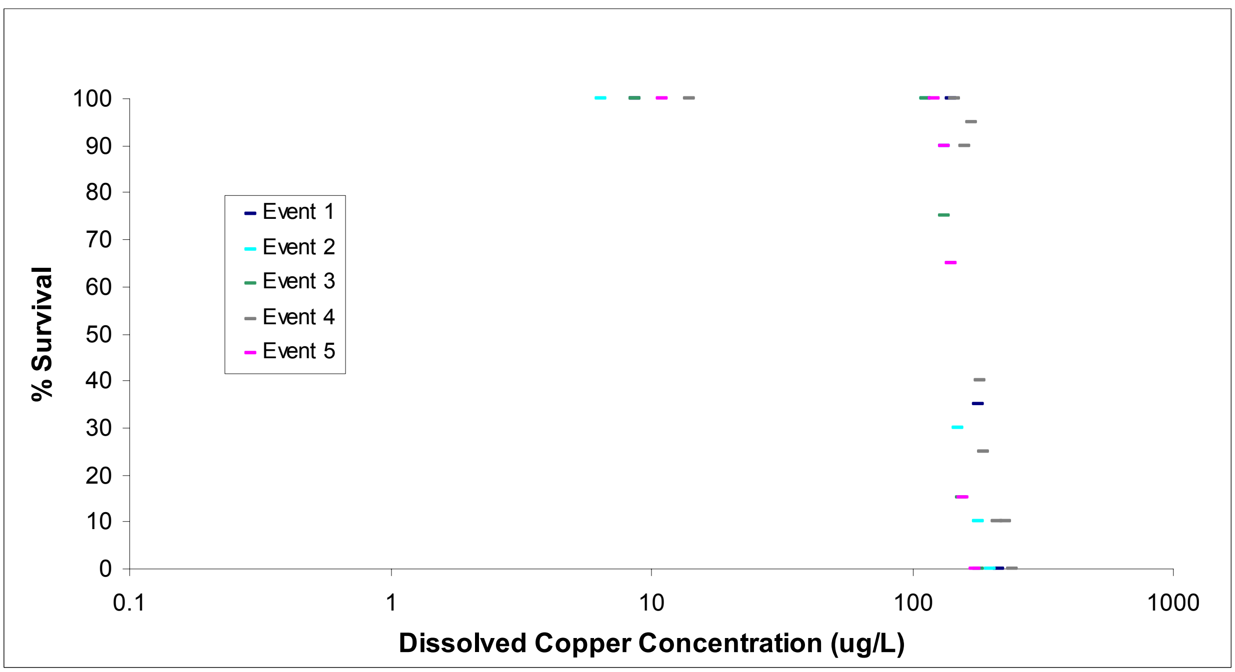

Figure 8. Concentration-Response Curves for Simulated Downstream Water (Sites G1 and R4) and Receiving Water (W1)
Hardness-normalized to 200 mg/L as $CaCO_3$

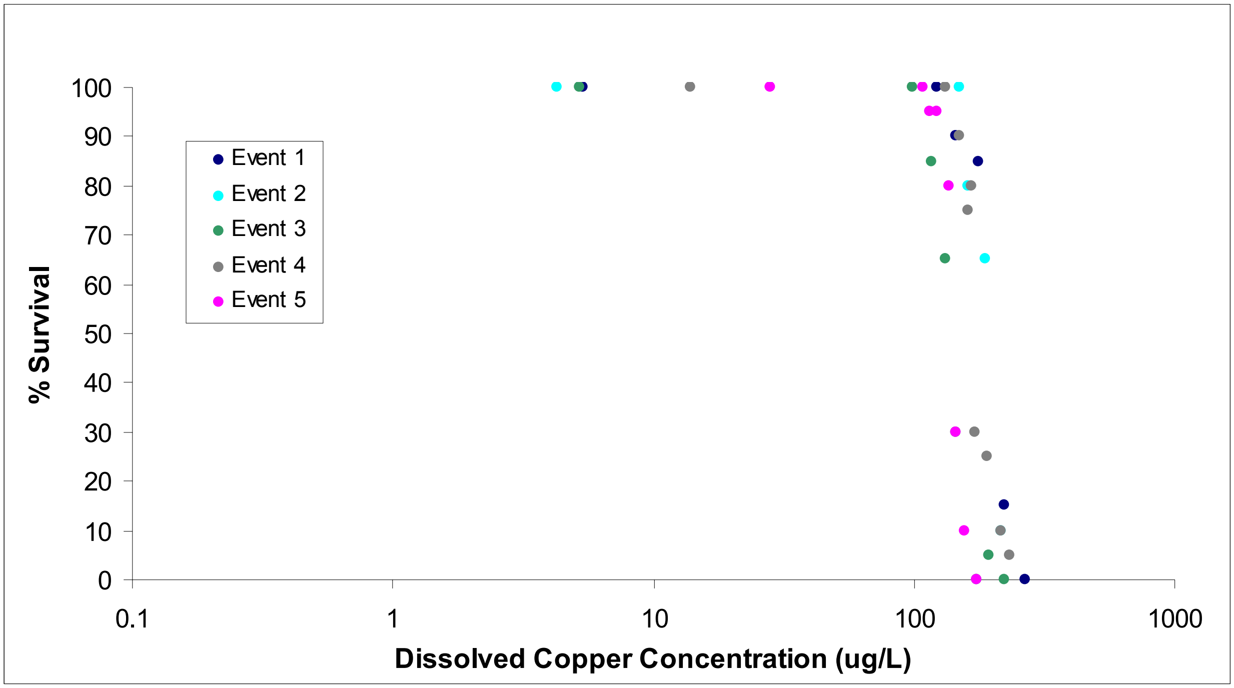

Figure 9. Concentration-Response Curves for Receiving Water Site LARR Hardness-normalized to 200 mg/L as $CaCO_3$

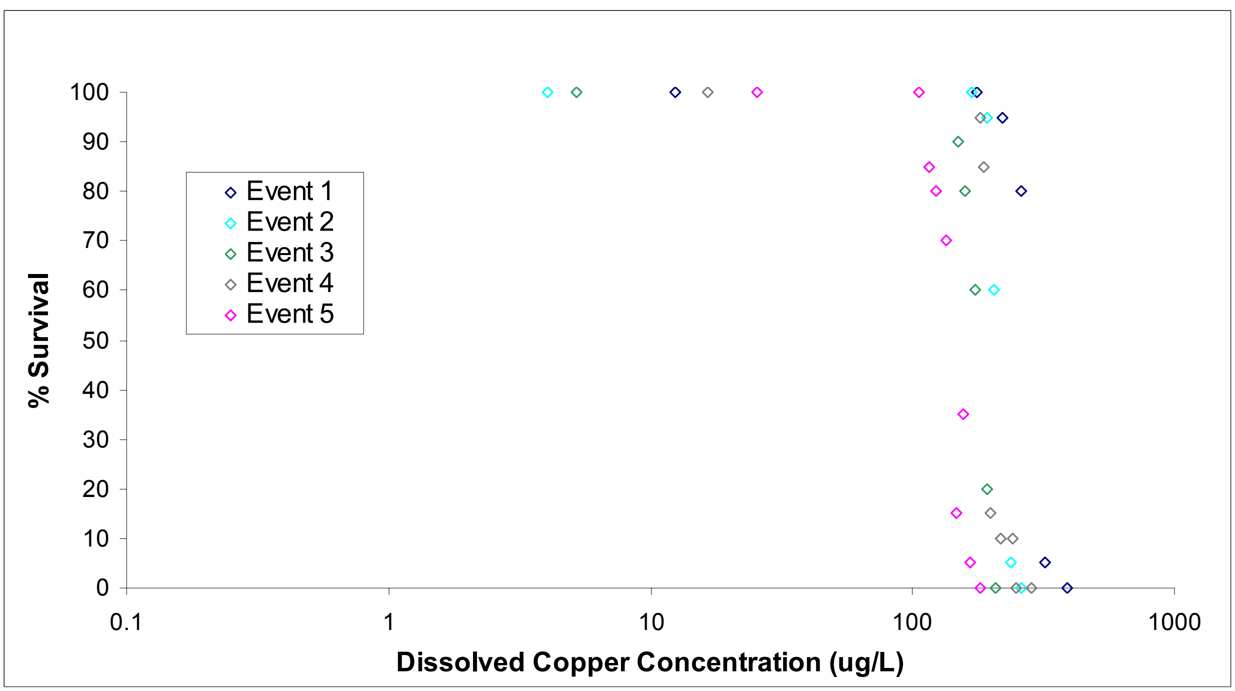

Figure 10. Concentration-Response Curves for Receiving Water Site LARW Hardness-normalized to 200 mg/L as $CaCO_3$

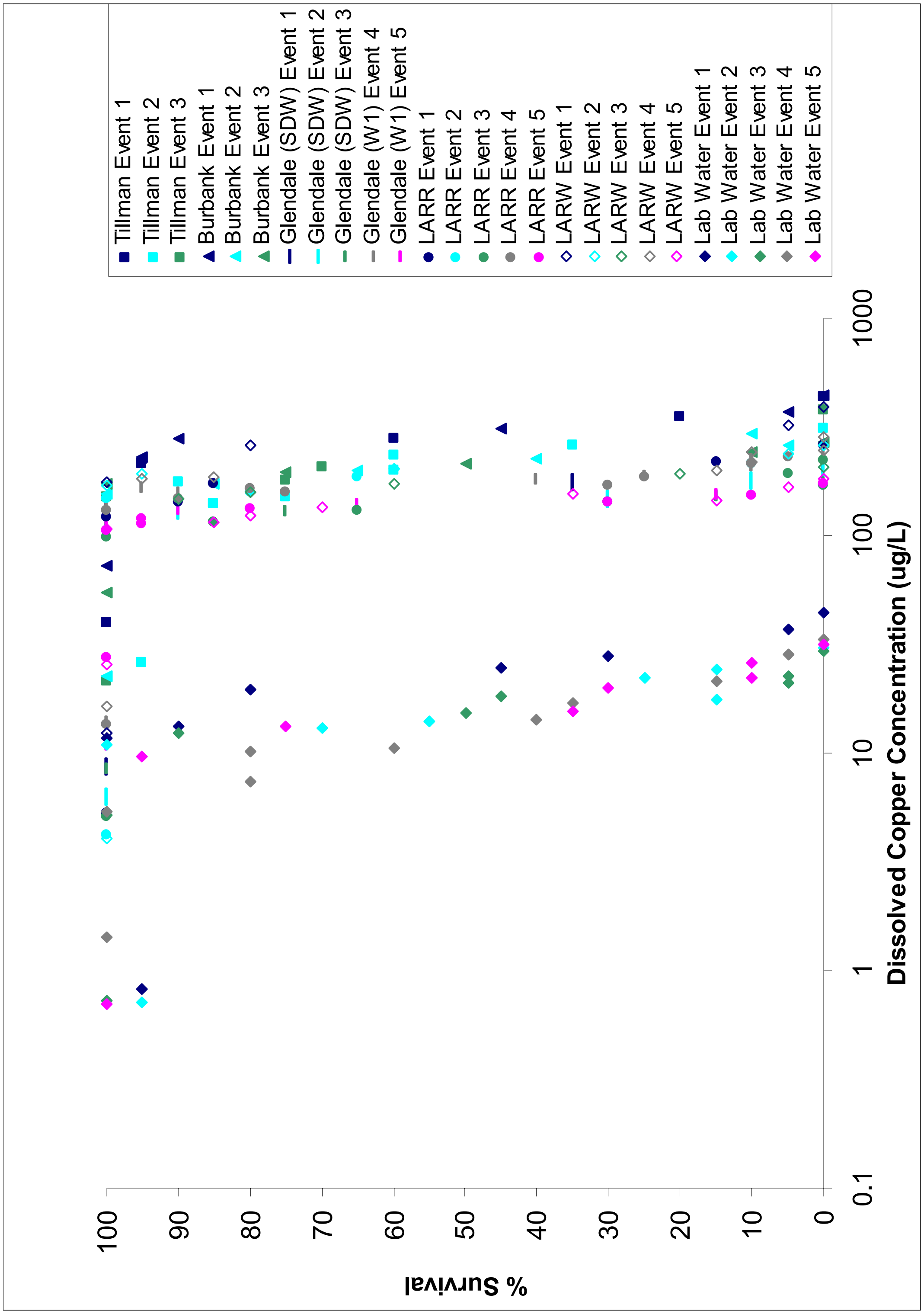

Figure 11. Concentration-Response Curves for All (Site and Lab Water) Hardness-normalized to 200 mg/L as $CaCO_3$

Table 30. Dissolved Copper EC50 Results for L.A. River Copper WER Study Site and Lab Water

Event	Sampling Site	Dissolved Cu EC50	Dissolved Cu EC50 95% confidence limits	Hardness	Hardness-normalized (200 mg/L as $CaC0_3$) Dissolved Cu EC50	Hardness-normalized (200 mg/L as $CaC0_3$) Dissolved Cu EC50 95% confidence limits
		(ug/L)	(ug/L)	(mg/L)	(ug/L)	(ug/L)
1	Lab Water	26.3	24.0 - 28.7	222	23.8	21.7 - 26.0
2		17.0	15.7 - 18.2	219	15.6	14.4 - 16.7
3		17.7	16.4 - 19.0	220	16.2	15 - 17.3
4		3.33	2.98 – 3.69	47.5	12.9	11.5 - 14.3
5		16.6	15.1 - 18.1	213	15.7	14.3 - 17.1
1	T1	190	176 - 205.3	124	299	277 - 322
2		170	158 - 183	141	236	220 - 254
3		226	209 - 245	185	243	224 - 264
1	B1	258	247 - 269	165	309	296 - 323
2		182	173 - 192	170	212	201 - 224
3		194	187 - 201	180	214	206 - 222
1	SDW[1]	200	191 - 209	238	170	162 - 177
2		167	160 - 174	230	146	140 - 152
3		163	156 - 169	235	140	134 - 145
4	W1	39.7	38.6 - 40.9	39.6	183	178 - 188
5		163	158 - 168	228	144	141 - 148
1	LARR	259	246 - 273	271	195	185 - 205
2		264	252 - 277	282	191	182 - 200
3		199	190 - 208	296	137	131 - 143
4		43.3	42.8 - 45.9	46.1	172	171 - 183
5		172	166 - 176	248	140	130 - 137
1	LARW	351	336 - 367	256	278	266 - 291
2		283	275 - 291	272	212	206 - 218
3		240	231 - 249	278	176	169 - 183
4		49.7	47.6 - 51.9	46.3	197	189 - 206
5		163	159 - 169	239	138	134 - 143

1 Simulated downstream water (SDW) using 7Q10 approach.

Note: The species mean acute value (SMAV) for *C. dubia* is 42.5 ug/L for dissolved copper, at a hardness of 200 mg/L (USEPA 2001). The SMAV is the geometric mean of the results of all acceptable acute toxicity tests for the most sensitive life stage of the species.

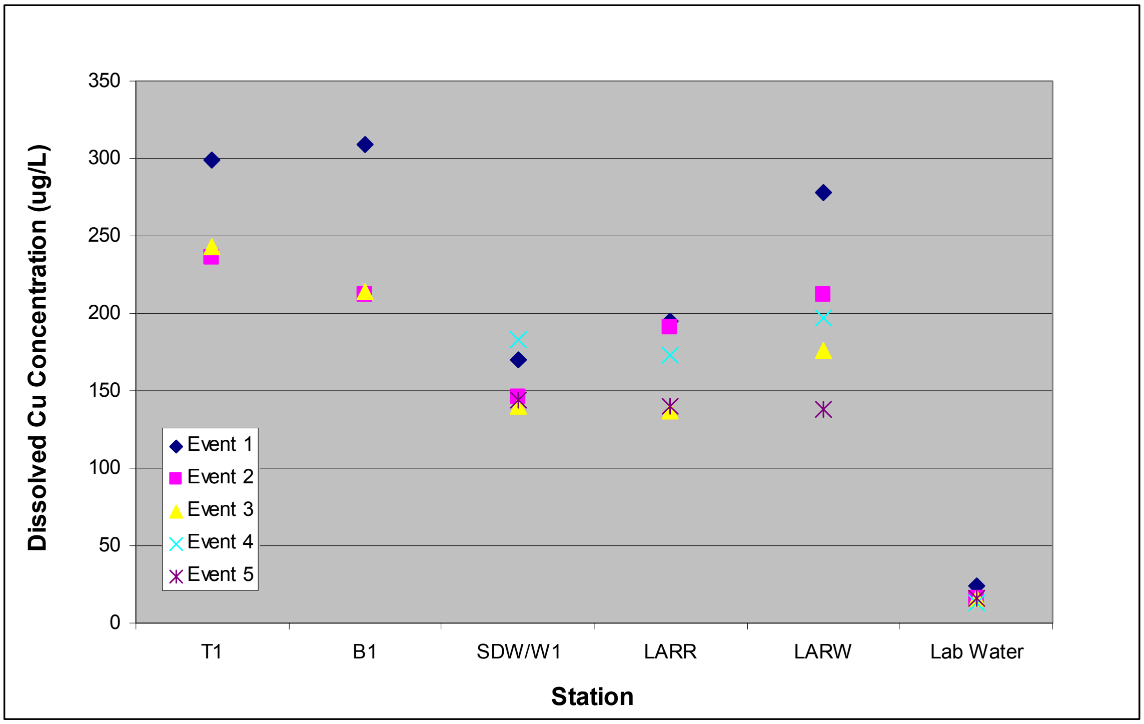

Figure 12. Site and Lab Water EC50s Hardness-normalized to 200 mg/L as $CaCO_3$

6.5 SAMPLE WATER-EFFECT RATIO CALCULATIONS

Table 31 presents a summary of sample water-effect ratios (sWER) calculated for Events 1 through 5 by site using the Interim Guidance and Streamlined Procedure calculation methods.

Interim Guidance sWER calculation method:

The sWER equals the site water EC50 divided by the lab-water EC50.

$$\text{sWER} = \frac{\text{Site Water EC50}}{\text{Hardness-normalized Lab Water EC50}}$$

Streamlined Procedure sWER calculation method:

a. If the lab water hardness-normalized EC50 is greater than the hardness-normalized Species Mean Acute Value (SMAV)[5] for copper, the sWER equals the site water EC50 divided by the lab water EC50.

$$\text{sWER} = \frac{\text{Site Water EC50}}{\text{Hardness-normalized Lab Water EC50}}$$

b. If the lab water, hardness-normalized EC50 is less than the hardness-normalized SMAV, the sWER equals the site water EC50 divided by the SMAV.

$$\text{sWER} = \frac{\text{Site Water EC50}}{\text{Hardness-normalized SMAV}}$$

The Streamlined Procedure calculation method (USEPA 2001) can result in a more conservative (lower) sWER because choosing the higher of the lab water hardness-normalized EC50 and the hardness-normalized SMAV will result in a larger denominator being used in the calculation, which results in a lower sWER. In all instances, sWERs calculated using the Streamlined Procedure method, presented in Table 31, resulted in lower sWERs than sWERs calculated using the Interim Procedure. The difference between sWERs calculated using the EC50 and the SMAV is due to differences in lab water EC50s and the SMAV. The SMAV for *C. dubia* at a hardness concentration equal to 200 mg/L as $CaCO_3$ is 42.5 ug/L (USEPA 2001). The SMAV value used was obtained from Appendix B of the Streamlined Procedure. The SMAV presented in the Streamlined Procedure was calculated by tabulating available toxicity data, normalizing for hardness differences using the 1985 and 1995 USEPA hardness slope for copper, and calculating the geometric mean of all EC50 results for each species.

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5 Species mean acute value" or "SMAV" means the geometric mean of the results of all acceptable flow-through acute toxicity tests (for which the concentrations of the test material were measured) with the most sensitive tested life stage of the species. For a species for which no such result is available for the most sensitive tested life stage, the SMAV is the geometric mean of the results of all acceptable acute toxicity tests with the most sensitive tested life stage.

Table 31. L.A. River Copper Sample Water-Effect Ratio (sWER) Calculations

Sampling Site	Dissolved Cu EC50 (95% Confidence Limit) (ug/L)	Hardness as $CaCO_3$ (mg/L)	Hardness-normalized (200 mg/L as CaC03) Dissolved Cu EC50 (95% Confidence Limit) (ug/L)	SMAV[2] Normalized to Standard Hardness (200 mg/L as CaC03) (ug/L)	sWER Calculated Using Interim Guidance Method[3]	sWER Calculated Using Streamlined Procedure Method[4]
Event 1 – August 2005						
T1	190 (176-205.3)	124	299 (277-322)	42.5	12.55	7.028
B1	258 (247-269)	165	309 (296-323)	42.5	12.99	7.274
SDW [1]	200 (191-209)	238	170 (162-177)	42.5	7.130	3.992
LARR	259 (246-273)	271	195 (185-205)	42.5	8.184	4.583
LARW	351 (336-367)	256	278 (266-291)	42.5	11.69	6.547
Lab Water	26.3 (24.0-28.7)	222	23.8 (21.7-26.0)	42.5	NA	NA
Event 2 – September 2005						
T1	170 (158-183)	141	236 (220-254)	42.5	15.14	5.562
B1	182 (173-192)	170	212 (201-224)	42.5	13.61	4.998
SDW [1]	167 (160-174)	230	146 (140-152)	42.5	9.370	3.442
LARR	264 (252-277)	282	191 (182-200)	42.5	12.24	4.496
LARW	283 (275-291)	272	212 (206-218)	42.5	13.57	4.986
Lab Water	17.0 (15.7-18.2)	219	15.6 (14.4-16.7)	42.5	NA	NA
Event 3 – October 2005						
T1	226 (209-245)	185	243 (224-264)	42.5	15.05	5.725
B1	194 (187-201)	180	214 (206-222)	42.5	13.22	5.030
SDW [1]	163 (156-169)	235	140 (134-145)	42.5	8.638	3.286
LARR	199 (190-208)	296	137 (131-143)	42.5	8.490	3.229
LARW	240 (231-249)	278	176 (169-183)	42.5	10.89	4.142
Lab Water	17.7 (16.4-19.0)	220	16.2 (15-17.3)	42.5	NA	NA
Event 4 – February 2006						
W1	39.7 (38.6-40.9)	39.6	183 (178-188)	42.5	14.15	4.298
LARR	43.3 (42.8-45.9)	46.1	172 (171-183)	42.5	13.37	4.062
LARW	49.7 (47.6-51.9)	46.3	197 (189-206)	42.5	15.29	4.644
Lab Water	3.33 (2.98-3.69)	47.5	12.9 (11.5-14.3)	42.5	NA	NA
Event 5 – March 2006						
W1	163 (158-168)	228	144 (141-148)	42.5	9.192	3.391
LARR	172 (166-176)	248	140 (130-137)	42.5	8.961	3.306
LARW	163 (159-169)	239	138 (134-143)	42.5	8.793	3.244
Lab Water	16.6 (15.1-18.1)	213	15.7 (14.3-17.1)	42.5	NA	NA

1 Simulated downstream water (SDW) comprised of LAG Effluent collected at site G1 and L.A. River water collected at R4 using 7Q10 approach.
2 The SMAV for *C. dubia* at a hardness equal to 200 mg/L is 42.5 ug/L (USEPA 2001).
3 Interim Guidance sWERs are calculated by dividing site water EC50 by the hardness-normalized lab-water EC50. For the purposes of comparing EC50s between events, site water EC50s and lab-water EC50s were normalization to a standard hardness of 200 mg/L $CaCO_3$.
4 Streamlined Procedure sWERs are calculated by dividing site water EC50 by the higher of the hardness-normalized lab-water EC50 and the hardness-normalized Species Mean Acute Value (SMAV). For the purposes of comparing EC50s between events, site water EC50s and the SMAV were normalization to a standard hardness of 200 mg/L $CaCO_3$.

6.6 INITIAL VERSUS FINAL COPPER CONCENTRATIONS

The Interim Guidance recommends that both initial and final copper measurements be made on all concentrations used in determining the EC50 endpoint. As outlined in the Work Plan, EC50 calculations were based on measured copper concentrations at the beginning of the test, rather than on final or time-weighted average of initial and final concentrations. The Work Plan followed initial versus final copper test sample analysis protocols established during previous studies because these protocols have been peer reviewed and approved by both the San Francisco Bay Technical Review Committees and USEPA specialists. The previous studies considered include:

- South San Francisco Bay Copper WER (San Jose 1998)
- New York/New Jersey Harbor Copper WER (SAIC 1993)
- San Francisco Bay North of Dumbarton Bridge Copper and Nickel WERs (EOA and LWA 2002)
- Calleguas Creek Watershed Copper WER (LWA 2006)

As outlined in the Work Plan, and supported by the studies presented above, it was believed that use of initial dissolved copper concentrations would result in the most appropriate EC50 calculations and WERs. However, to evaluate whether the use of initial concentrations (as opposed to final concentrations) had the potential to affect the calculations of EC50s and WERs, the copper concentrations in the WER toxicity tests were analyzed using a simple regression to evaluate how well the final dissolved copper concentrations were predicted by the initial concentrations. This was followed by an evaluation of the percent change from initial to final copper concentration as a function of the average concentration for the test.

As illustrated in Figure 13, final dissolved copper concentrations are very well predicted by the initial concentrations. One outlier result was excluded from the regression analysis due to apparent contamination of the final copper measurement. The R-squared value for the regression was 0.988. The slope of the regression was 0.991 and was not significantly different from a slope of 1.0 (*i.e.*, it did not depart significantly from equality), and the intercept for the regression was not significantly different from zero. Regression statistics are provided in Table 32. The results of evaluation of the percent change in copper concentrations (Figure 14) show that percent change is centered around zero and most of the results lie within 25% of the average concentration for each sample, which is the acceptable limit for analytical variability between replicate analyses. The larger percent deviations are at lower concentrations and include most of the laboratory control samples and unspiked environmental samples. One cluster of results that deviate from this overall pattern are the Event 4 wet weather samples for LARR, LARW, and W1. This group of results exhibited a consistent decrease which suggests that the higher particulate concentrations observed during this storm event required a longer period to equilibrate and that using initial copper concentrations may have resulted in higher WERs for these sites for this event. For the dry weather events that are used to calculate the final WERs, there is no indication of bias and no expectation that WERs calculated with the initial copper measurement for a toxicity test would differ significantly or systematically from WERs calculated with the final measurement or with the average measurement.

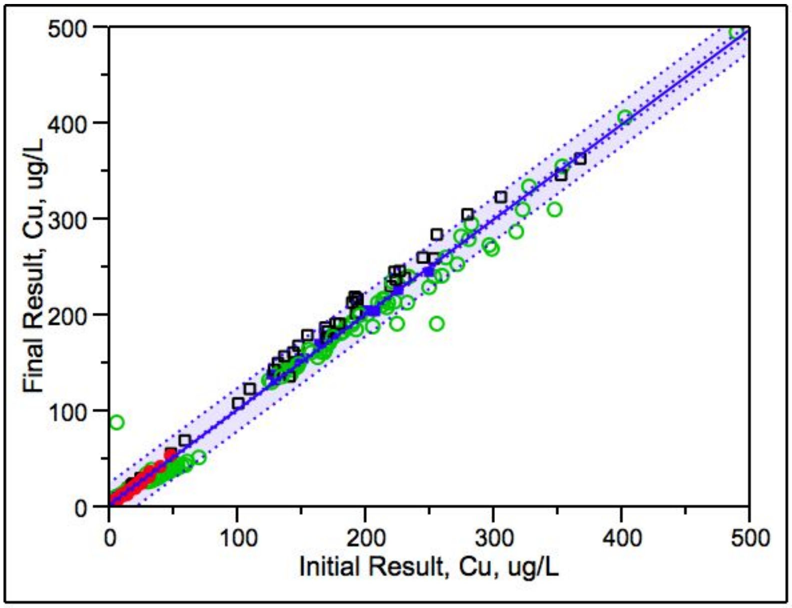


Figure 13. Regression of Final versus Initial Dissolved Copper Concentrations in WER Toxicity Tests

Note: Shaded region indicates 95% CI for individual results predicted by the regression;
Red filled circles = labwater samples; Black open squares = effluent samples;
Green open circles = ambient receiving water; Blue filled squares = simulated downstream water;
One outlier result was excluded from the regression analysis due to apparent contamination of the final copper measurement.

Table 32. Regression Statistics: Final versus Initial Dissolved Copper Concentrations

Summary of Fit					
Regression R-Square	0.988				
Observations	193				
p-value for regression model	<0.0001				
Parameter Estimates					
Term	**Estimate**	**Lower 95%**	**Upper 95%**	**Std Error**	**Prob>|t|**
Intercept	-0.987	-3.47	1.50	1.26	0.4346
Initial Dissolved Copper	0.991	0.976	1.01	0.008	<.0001

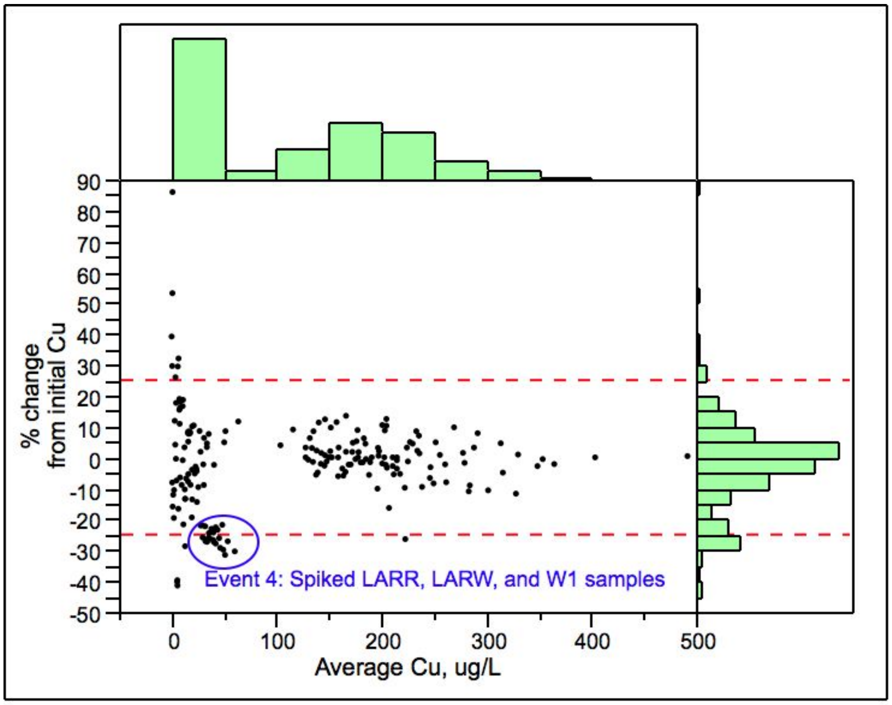


Figure 14. Percent Change from Initial to Final Copper Result

6.7 TOXICITY STATISTICAL ANALYSES

Understanding variability in sWERs is important in determining how to group data to calculate the final WER (fWER), as discussed in the following section. Toxicity statistical analyses are used to answer the following key questions identified in Section 1.2 (Study Objective) and ultimately determine appropriate fWERs:

- Is dry weather the critical condition for copper in the L.A. River?
- Are there differences in WERs between reaches of the L.A. River?
- If there are differences in WERs between reaches of the L.A. River, are any reaches similar?

Statistical differences between events and sites were evaluated using sWERs calculated with lab water EC50s (instead of the hardness-normalized SMAV). sWERs based on lab water EC50s provide a more objective basis for these comparisons because they are not biased by additional policy-based factors introduced with SMAV-derived WERs. However, the Streamlined Procedure, which requires calculation of the sWER using the higher of the lab water EC50 or SMAV, will ultimately be used to calculate the final WER (fWER) per the Final Work Plan (LWA 2005).

Events 1, 2, and 3 were conducted to represent similar dry season dry weather conditions. Events 4 and 5 were conducted to represent two different wet season conditions: wet season wet weather and wet season dry weather, respectively. Events 1, 2, 3, and 5 occurred during dry weather conditions. Event 4 occurred during wet weather conditions. To determine whether dry or wet weather constituted a critical condition based on sWERs (*i.e.*, lower sWERs), a two-way analysis of variance (ANOVA) analysis was conducted on the sWERs. The ANOVA analysis was conducted on the three sites that had both dry and wet weather data (SDW/W1, LARR, and LARW). The ANOVA analyzed for significant differences between the dry and wet weather sWERs for each site. Table 33 presents the ANOVA analysis results. ANOVAs using only the three sites analyzed for all events (SDW/W1, LARR, and LARW) clearly showed a significantly lower sWER for dry weather events. Wet event samples resulted in statistically significantly[6] higher sWERs than dry events; therefore dry weather is critical condition. Analysis indicates that sites should be analyzed for differences based on dry weather samples. Additionally, no significant site differences were identified for the sites (SDW/W1, LARR, and LARW) at alpha = 0.05 for this analysis. The analysis demonstrates that dry weather is the critical condition based on sWERs.

Table 33. sWER Two-Way Analysis Of Variance (ANOVA) Results of Dry and Wet Events for Three L.A. River Copper WER Study Sites (SDW/W1, LARR, and LARW)

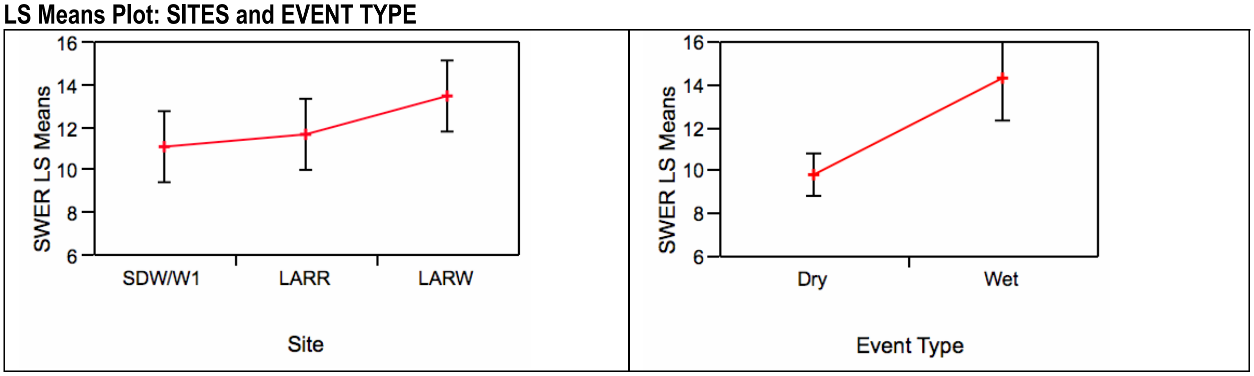
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	64.0	21.3	8.82
Error	11	26.6	2.42	**Prob > F**
C. Total	14	90.6		0.0029

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Site	2	2	15.4	3.19	0.081
Event Type	1	1	48.6	20.1	0.001

LS Means Plot: SITES and EVENT TYPE



LSMeans Differences Student's t for EVENT TYPE

alpha=0.05 t=2.20; Levels not connected by same letter are significantly different.

Level			Least Sq Mean
Wet	A		14.27
Dry		B	9.77

To determine if there were differences in sWERs between sites, an ANOVA analysis was conducted with all sites (T1, B1, SDW/W1, LARR, and LARW) for the three season dry weather events. This initial ANOVA analysis was conducted for dry season dry weather events only because dry weather was identified as the critical condition in the previous analysis. A second ANOVA was also conducted with all dry weather events. T1 and B1 were sampled only during dry season dry weather events (Events 1, 2, and 3), so the

[6] The threshold of statistical significance was set at the 95% confidence level (p<0.05) for all tests. Therefore, p-values less than 0.05 indicate that a factor had a significant effect on the sWER, at a 95% confidence level.

model is slightly “unbalanced”. Including data for Event 5, which was only conducted at SDW/W1, LARR, and LARW, supported the conclusions from the ANOVA for dry season events.

The results of the ANOVA analyses indicate there are some statistically significant differences between individual dry weather sWERs at each individual site from event-to-event. T1 and B1 have similar site characteristics and are not statistically different in the initial ANOVA analysis (Table 34). Based on these results and spatial relationship among sites and reaches, the analysis indicates that the L.A. River sites should be analyzed separately to determine whether there are significant site differences. Table 35 presents the ANOVA analysis results.

Table 34. sWER Two-Way Analysis Of Variance (ANOVA) Results of All L.A. River Copper WER Study Sites (T1, B1, SDW/W1, LARR, and LARW) for Dry Season Dry Weather Events (Events 1, 2, and 3)

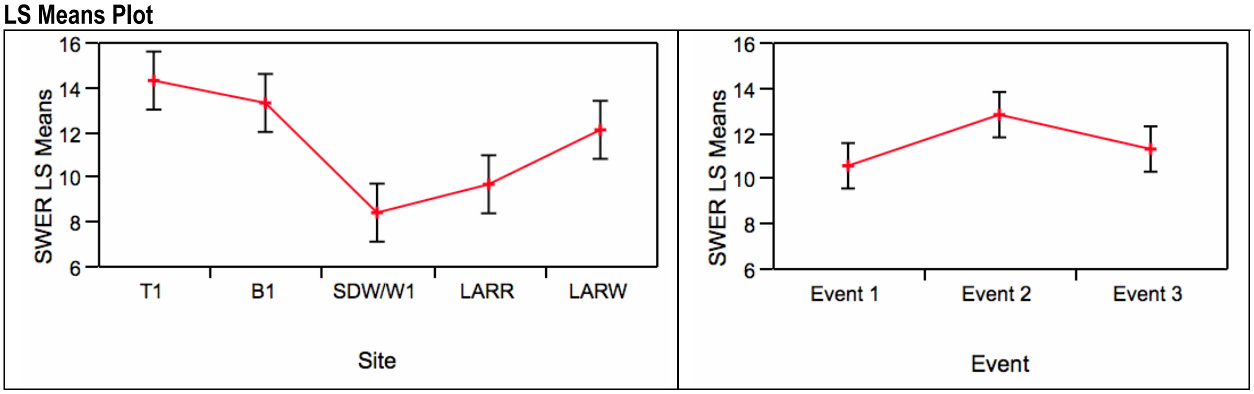
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	6	86.5	14.4	15.22
Error	8	7.58	0.947	**Prob > F**
C. Total	14	94.0		0.0006

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Event	2	2	13.3	7.008	0.0174
Site	4	4	73.2	19.32	0.0004

LS Means Plot



LSMeans Differences Tukey HSD: SITES

alpha=0.050 Q=3.45476; Levels not connected by same letter are significantly different.

Level				Least Sq Mean
T1	A			14.3
B1	A			13.3
LARW	A	B		12.4
LARR		B	C	9.6
SDW/W1			C	8.4

LSMeans Differences Tukey HSD: EVENTS

alpha=0.050 Q = 2.85742; Levels not connected by same letter are significantly different.

Level			Least Sq Mean
Event 2	A		12.8
Event 3	A	B	11.3
Event 1		B	10.5

Table 35. sWER Two-Way Analysis Of Variance (ANOVA) Results of All L.A. River Copper WER Study Sites (T1, B1, SDW/W1, LARR, and LARW) for All Dry Weather Events (Events 1, 2, 3, and 5)

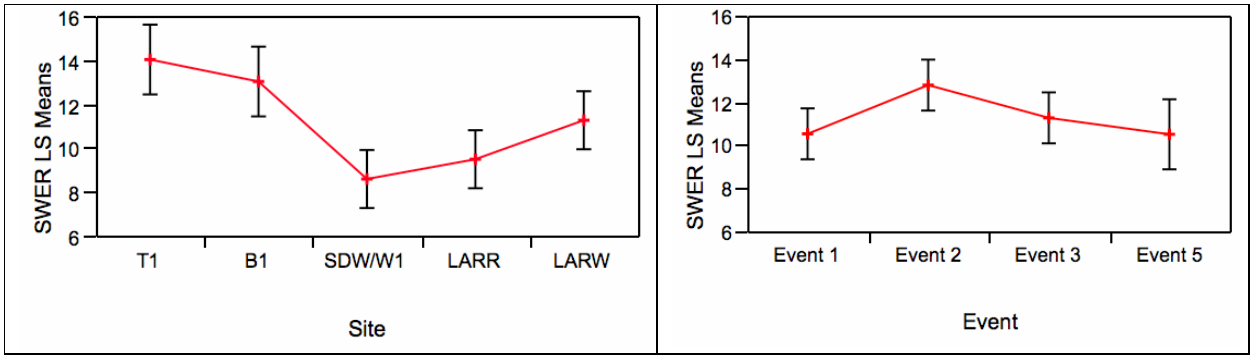
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	7	95.9	13.7	9.76
Error	10	14.1	1.41	**Prob > F**
C. Total	17	110		0.0009

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Site	4	4	66.8	11.9	0.0008
Event	3	3	15.6	3.71	0.0500

LS Means Plot



LSMeans Differences Tukey HSD: SITES

alpha=0.050 Q=3.29108; Levels not connected by same letter are significantly different.

Level			Least Sq Mean
T1	A		14.0
B1	A		13.0
LARW	A	B	11.3
LARR		B	9.48
SDW/W1		B	8.58

LSMeans Differences Tukey HSD: EVENTS

alpha=0.050 Q = 3.05936; Levels not connected by same letter are significantly different.

Level		Least Sq Mean
Event 2	A	12.8
Event 3	A	11.3
Event 1	A	10.5
Event 5	A	10.5

The initial ANOVA analyses indicated that there was no statistically significant difference between T1 and B1 sWERs, but there was a statistically significant difference between these two sites and the remaining three sites (SDW/W1, LARR, and LARW). The two-way ANOVA analyses conducted including all four dry weather condition events (Events 1, 2, 3, and 5) for all sites indicated no statistically significant differences in sWERs between dry weather events (Table 35). The subsequent one-way analysis indicated no statistically significant differences in sWERs exist between SDW/W1, LARR, and LARW during dry weather events (Table 36). The seemingly increasing sWER trend with distance downstream is not significant ($p<0.05$). Separate two-way and one-way ANOVA analysis of dry weather results for T1 an B1 confirmed no statistically significant differences between events or between these sites. The final one-way analysis of differences between T1 and B1 is presented in Table 37.

Table 36. sWER Two-Way Analysis Of Variance (ANOVA) Results of L.A. River Copper WER Study Sites SDW/W1, LARR, and LARW for All Dry Weather Events (Events 1, 2, 3, and 5)

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	14.8	7.41	2.63
Error	9	25.3	2.81	**Prob > F**
C. Total	11	40.1		0.126

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
SDW/W1	8.58	0.84	8.58
LARR	9.48	0.84	9.48
LARW	11.3	0.84	11.3

LS Means Plot

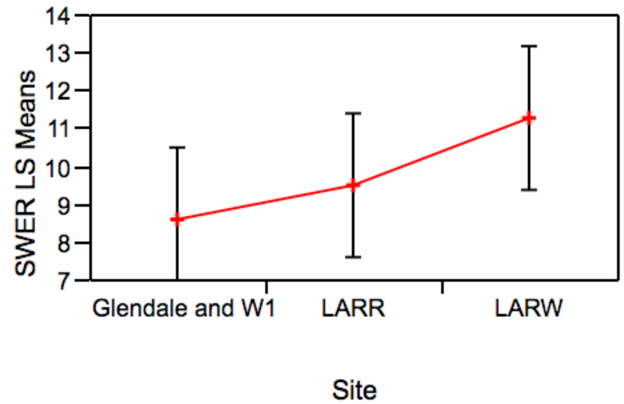


Table 37. sWER One-Way Analysis Of Variance (ANOVA) of L.A. River Cu WER Study Sites T1 and B1 for All Dry Weather Events (Events 1, 2, and 3)

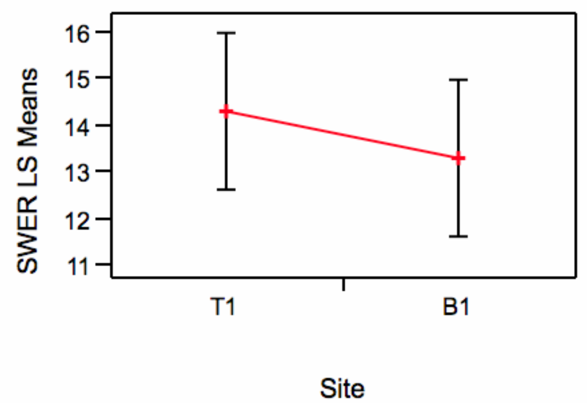
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1.50	1.50	1.378
Error	4	4.35	1.09	Prob > F
C. Total	5	5.85		0.3055

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
T1	14.3	0.60	14.3
B1	13.3	0.60	13.3

LS Means Plot



In summary, potential variations in sWERs were evaluated to determine any difference in both site location and weather conditions. The various ANOVA analyses indicated the following:

- Wet vs. Dry Weather: Evaluation of wet and dry weather conditions indicates that there is a statistically significant difference between sWERs for dry weather (Events 1, 2, 3, and 5) and wet weather (Event 4). The wet weather event sWER is higher, which supports the conclusion that dry weather is the critical condition.
- Dry Weather Event to Event: There are no statistically significant differences between individual dry weather sWERs (Events 1, 2, 3, and 5) at each site.
- T1 vs. B1 sWERs: There are no statistically significant differences between T1 and B1 sWERs but there are statistically significant differences between these two sites and the other sampling sites.
- SDW/W1 vs. LARR vs. LARW sWERs: There are no statistically significant differences between the sWERs for SDW/W1, LARR, and LARW during the four dry weather condition events (Events 1, 2, 3, and 5).
- Increasing sWER Trend: The seemingly increasing sWER trend with distance downstream is not significant ($p<0.05$).

6.8 INVESTIGATION OF WERs LARGER THAN FIVE

Section I part 7 of the Interim Guidance discusses investigating WER results. Subsection c states that if a WER is larger than five, it should be investigated. The following three avenues of investigation are suggested:

7(c) 1. If the endpoint obtained using the laboratory dilution water was lower than previously reported lowest value or was more than a factor of two lower than an existing Species Mean Acute Value in a criteria document, additional tests in the laboratory dilution water are probably desirable.

7(c) 2. If a total recoverable WER was larger than five but the dissolved WER was not, is the metal one whose WER is likely to be affected by TSS and/or TOC and was the concentration of TSS and/or TOC high? Was there a substantial difference between the total recoverable and dissolved concentrations of the metal in the downstream water?

7(c) 3. If both the total recoverable and dissolved WERs were larger than 5, is it likely that there is nontoxic dissolved metal in the downstream water?

Aside from conducting an investigation, it should be noted the Interim Guidance does not indicate what to do with WERs larger than five based on the results of the investigation. Of the 21 sWERs presented in Table 31, five calculated utilizing the Streamlined Procedure and 21 calculated utilizing the Interim Guidance were larger than five. The Streamlined Procedure does not contain a provision to conduct an investigation of WERs larger than five. This is likely partially due to the acknowledgement within the Streamlined Procedures that POTWs commonly exceed the national copper criterion while actual toxicity due to copper from such facilities is rare because of the higher than average presence of complexing organics. Further, the Interim Guidance was developed before a number of site-specific studies were conducted. As such, there were concerns that site-specific criteria might be larger than appropriately protective because of variability or error in toxological measurements. Lab water EC50s calculated in site-specific studies could be significantly lower than those used in development of the criteria, which could drive up the value of the WER, hence the requirement in the Streamlined Procedure to use the larger of the lab water EC50 or SMAV to calculate the WER.

An initial review of available information on WER studies conducted around the nation indicates that freshwater copper WERs commonly exceed five. Table 38 presents a summary of the references reviewed. These data would not have been available for consideration during the development of the Interim Guidance.

Table 38 Results of Freshwater WER Studies for Development of Copper WERs

Water-Effect Ratios Presented	Location	Reference
0.98 to 12.53	States of AZ, CA, CO, NM, NV, and OR	Parametrix 2006
2.07 to 8.39	Texas	USEPA 2008
14.7	Quinnipiac River Basin, CN	Connecticut DEP 1996 as cited in Hall et. al 1997

6.8.1 Comparison of Lab Water EC50s to SMAV

The following section evaluates whether the endpoint obtained using the laboratory dilution water was lower than previously reported lowest value, was more than a factor of two lower than an existing SMAV in a criteria document, and if so, whether it has any meaning with regard to calculating WERs for the L.A. River. Additionally, the Interim Guidance indicates that a comparison of test results between laboratories provides a check on all aspects of the test procedure. Furthermore, acceptability of dilution water (or lab water in the case of this Study) must be evaluated by comparing lab water results obtained through this Study to comparable lab dilution water used in other relevant studies. If the results differ by more than a factor of 1.5 from the values from the other studies, new and old data must be evaluated to determine whether the lab water used in the WER determination is acceptable. The EC50s from various studies used to calculate the SMAV presented in the Streamlined Procedure may be used as results from comparable studies. The difference between hardness-normalized lab water EC50s and the hardness-normalized SMAV, presented in Table 31, is greater than a factor of 1.5 for all five events with an average difference of 2.6. The authors of the Streamlined Procedure noted that such differences are fairly common and that the lab-water EC50s are usually less than the SMAV while still within a reasonable range. The lab water EC50s do fall within the observed range of EC50s used to calculate the SMAV. However, the lab water EC50s do not fall within the upper and lower 95% confidence limits of the SMAV EC50 data (mean = to 56.2 upper and lower CL = 45.7-66.8 ug/L). Note that the lab water EC50s are closer to the upper and lower 95% confidence limits (mean = to 23.9 upper and lower CL = 18.7-29.1 ug/L) of the more recent EC50 data (post 1990) used to calculate the SMAV.

The differences between the lab water EC50s and SMAV may be partly attributed to differences in the lab water used in this Study and waters used in development of the SMAV (*e.g.*, natural vs. lab water) and partly due to differences in sensitivity of test organisms used in this Study. Table 39 presents a summary of hardness-normalized lab water EC50s and hardness-normalized SMAV presented in Table 31.

The hardness normalized data, presented in Table 31 and Table 39 are generated using the hardness relationship presented in the CTR. However, other constituents that affect copper toxicity may have been present in lab waters used to generate the SMAV that were not present in the lab water used in this Study. As described in Section 4.2, lab water used in this Study was reconstituted water created according to USEPA guidance. Lab waters used in developing the SMAV included "natural" waters obtained from lakes that may have higher levels of constituents that affect copper toxicity, such as DOC, that were not present at comparable levels in the lab water used in this Study. To evaluate the potential effect of other constituents on differences between lab water EC50s and the SMAV, the BLM was used to "BLM-normalize" lab water EC50 and SMAV data. Normalization using the BLM allows for a comparison using a more robust set of parameters that affect copper toxicity than simply using hardness-normalization. Similar to choosing a standard hardness (200 mg/L as $CaCO_3$) for normalization, BLM parameters are set to reference exposure conditions. The reference exposure conditions are presented in the Copper Criteria Document and are based on the USEPA formulation for moderately-hard reconstituted water: temperature = 20°C, pH = 7.5, DOC = 0.5 mg/L, Ca = 14.0 mg/L, Mg = 12.1 mg/L, Na = 26.3 mg/L, K = 2.1 mg/L, SO_4 =81.4 mg/L, Cl = 1.90 mg/L, Alkalinity = 65.0 mg/L and S = 0.0003 mg/L.

Table 39 also presents the results of BLM-normalized lab water EC50s and BLM-normalized SMAV. The difference between BLM -normalized lab water EC50s and SMAV is greater than a factor of 1.5 for all five events with an average difference of 2.3, which is slightly better than the hardness-normalization.

Table 39. Summary of Hardness-normalized and BLM-normalized Lab Water EC50s and SMAV

Event	Dissolved Cu EC50	Hardness Normalization			BLM Normalization	
		Hardness as CaCO3	Dissolved Cu EC50 for Lab Water Normalized to Standard Hardness of 200 mg/L as CaC03	SMAV[1] Normalized to Standard Hardness of 200 mg/L as CaC03	Dissolved Cu EC50 for Lab Water BLM-normalized	SMAV[2] BLM-normalized
	(ug/L)	(mg/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
1	26.3	222	23.8	42.5	2.26	5.93
2	17	219	15.6		1.12	
3	17.7	220	16.2		2.96	
4	3.33	47.5	12.9		14.3	
5	16.6	213	15.7		4.85	

1 The SMAV for *C. dubia* at a hardness equal to 200 mg/L as $CaCO_3$ is 42.5 ug/L (USEPA 2001).
2 The SMAV for *C. dubia* at the reference exposure conditions in the BLM is 5.93 ug/L (USEPA 2007).

The difference between lab water EC50s and SMAV (in both hardness- and BLM-normalized scenarios) may be partly attributed to differences in the lab water used in this Study and lab waters used in development of the SMAV (*e.g.*, natural vs. lab water) and partly due to a difference in the test organism sensitivity in this Study. The difference in test organism sensitivity may result in lower EC50s in the site and lab water, as more sensitive organisms would respond at lower copper concentrations. Lower EC50s may result in an artificially high WER because lower lab water EC50s result in higher WERs as shown in the equation below.

$$sWER = \frac{\text{Site Water EC50}}{\text{Hardness-normalized Lab Water EC50}}$$

However, using the SMAV to calculate WERs, as opposed to using lab water EC50s, addresses the potential for an artificial inflation of WER values caused by differences in the lab water and/or species sensitivity. The authors of the Streamlined Procedure noted concern about the values of the lab-water EC50 used for calculating WERs as lab water EC50s, which are typically within a reasonable range, are usually less than the SMAV. The lower lab water EC50s would create a slight bias toward increasing the WER. The potential for high biasing the WER was intended to be eliminated in the Streamlined Procedure by requiring that the greater of the lab water EC50 or the SMAV be used in the WER calculation. As noted in the Streamlined Procedure, “This stipulation tends to slightly depress the WER under the Streamlined Procedure.” The issue of whether the difference between lab water EC50s and SMAV is attributable to differences in the lab and/or partly due to test organism sensitivity can not be completely resolved in this Study. Regardless, use of the Streamlined Procedure (*i.e.*, higher of the lab water or SMAV in calculating WERs) will result in WERs and subsequent MCOs that are as or more protective than intended by the water quality criteria.

6.8.2 Evaluation of Section I, parts 7(c) 2 and 7(c) 3

Parts 7(c) 2 and 7(c) 3 evaluate both total and dissolved WERs larger than five:

7(c) 2. If a total recoverable WER was larger than five but the dissolved WER was not, is the metal one whose WER is likely to be affected by TSS and/or TOC and was the concentration of TSS and/or TOC high? Was there a substantial difference between the total recoverable and dissolved concentrations of the metal in the downstream water?

7(c) 3. If both the total recoverable and dissolved WERs were larger than 5, is it likely that there is nontoxic dissolved metal in the downstream water?

Only dissolved WERs were developed per the Work Plan (LWA 2005) as allowed by the Streamlined Procedure and as determined in conjunction with the TAC and Regional Board. As such, a comparison between total and dissolved WERs is not applicable to this study.

6.8.3 Summary

The use of the Streamlined Procedure approach to calculate the WERs (i.e., utilizing the higher of the lab water hardness-normalized EC50 and the hardness-normalized SMAV) addresses the potential for an artificial inflation of WER values caused by differences in the lab water and/or species sensitivity. Further, use of the Streamlined Procedure approach to calculate the WERs overcomes concerns in the Interim Procedure about using the too low lab water EC50s to derive too high WERs (i.e., WERs larger than five). The potential for high biasing the WER was intended to be eliminated in the Streamlined Procedure by requiring that the greater of the lab water EC50 or the SMAV be used in the WER calculation.

The number of WERs derived and their spatial and temporal consistency based on the Interim Guidance and Streamlined Procedures as presented in Table 31 procedures are compelling. The concerns related to deriving site-specific criteria using limited data sets (as expressed in the requirements to investigate WER results in the Interim Guidance) are not applicable given the extensive database developed in this study. Finally, the multiple tests of effluent and downstream sites, the spatial and temporal stability of site water EC50s and sWERs, and use of the more recent Streamlined Procedure requirements for appropriate lab water should alleviate concerns over the possible presence of unexpected and unquantified factors that might affect the biological availability of copper.

7 CALCULATION OF RECOMMENDED WER AND MCO

7.1 CRITICAL CONDITION

All available information was considered to determine if a critical condition could be identified. As discussed previously, statistical difference between events and sites were evaluated. The sWERs for each individual site were not statistically different for the four dry weather condition sampling events (Events 1, 2, 3, and 5) indicating that the within site sWERs should be the same under dry weather conditions when the LA River is experiencing low flows. The sWERs for wet weather (Event 4) were significantly higher statistically than dry weather sWERs. Additionally, dissolved copper concentrations were higher during dry weather (Table 40). Lastly, flow in the L.A. River (Table 41) was significantly higher during the wet weather event (Event 4). The increase in flow combined with lower dissolved copper concentrations indicates a higher assimilative capacity for copper during wet weather. This suggests that dry weather conditions represent the critical condition for aquatic life protection from copper in the study area (*e.g.*, lowest sWER, more biologically available copper, and lowest flow volume available for dilution).

As noted earlier, there is significant variability in copper concentrations in the BWRP effluent. Additionally, concentrations at LARR and LARW were significantly higher during Event 5. It is not clear why copper concentrations were higher in Event 5; however, the additional copper loading may be due to discharges from upstream tributaries and/or urban runoff. Regardless, the elevated copper concentrations do not affect WER calculations.

Table 40. Dissolved Copper Concentrations (ug/L) Measured During Sampling Events for the L.A. River Copper WER

Event #	T1	B1	SDW[1]	W1	LARR	LARW
1	28.6	65.5	11.5	---	8.14	9.09
2	22.1	17.4	8.68	---	7.09	6.44
3	24.7	55.9	11.5	---	8.87	12.9
4	---	---	---	2.63	3.13	3.59
5	---	---	---	14.2	38.7	33.9

--- Dashed line indicates samples were not collected at this site during the event.
1 Simulated downstream water (SDW) using 7Q10 approach.

Table 41. Average Flow Rate in the L.A. River During Each Sampling Event (cfs)[1,2]

Event #	W1[1]	LARR[2]	LARW[3]
1	---	105	134
2	---	118	134
3	---	97	144
4	4,468	10,335	14,071
5	138	155	186

--- Dashed line indicates flow measurements were not collected at this site during the event.
1 Event 4 flows were obtained from the flow gage located at Tujunga Boulevard eight miles upstream of W1. Event 5 flows were measured in the river by field staff.
2 Event 1, 2, 3, and 5 flows were measured in the river by field staff. Event 4 flows were obtained from the flow gage located at Firestone Boulevard approximately three miles upstream of LARR.
3 LARW flows were obtained from the flow gage located at Wardlow Road approximately one mile upstream of LARW.

7.2 SAMPLE WATER-EFFECT RATIO CALCULATION FOR USE IN FINAL WATER-EFFECT RATIO CALCULATION

The Streamlined Procedure WER calculation method is used for generating sWERs that are used in calculating the final WER (fWER) for each site. Through the use of the higher of the lab water EC50 and SMAV the Streamlined Procedure eliminates the potential for variability and bias associated with use of only the lab water EC50 as outlined in the Interim Procedure and is expected to provide more stable results than the Interim Procedure (USEPA 2001). The use of the Streamlined Procedure can be expected to yield a criterion as protective as, or more protective than, that intended by the National WQC Guidelines for chemical-specific criteria. Table 42 presents a summary of the sWERs calculated for Events 1-5 by site using the Streamlined Procedure. sWERs were calculated for each event for site water using the following approach outlined in the Streamlined Procedure:

Calculate the sWER from copper toxicity test values normalized to the same hardness.

a. If the lab water hardness-normalized EC50 is greater than the hardness-normalized SMAV for copper, the sWER equals the site water EC50 divided by the hardness-normalized lab water EC50.

$$\text{sWER} = \frac{\text{Site Water EC50}}{\text{Hardness-normalized Lab Water EC50}}$$

b. If the lab water hardness-normalized EC50 is less than the hardness normalized SMAV, the sWER equals the site water EC50 divided by the hardness-normalized SMAV.

$$\text{sWER} = \frac{\text{Site Water EC50}}{\text{Hardness-normalized SMAV}}$$

Table 42. L.A. River Copper sWERs Summary Calculated Using the Streamlined Procedure

Sampling Site	sWER				
	Dry Season			Wet Season	
	Event 1	Event 2	Event 3	Event 4	Event 5
T1	7.028	5.562	5.725	---	---
B1	7.274	4.998	5.030	---	---
SDW[1]	3.992	3.442	3.286	---	---
W1	---	---	---	4.298	3.391
LARR	4.583	4.496	3.229	4.062	3.306
LARW	6.547	4.986	4.142	4.644	3.244

--- Dashed line indicates samples were not collected at this site during the event.
1 Simulated downstream water (SDW) created using 7Q10 approach.

Table 43 presents a summary of sWERs calculated using the Interim Guidance to contrast the Streamlined Procedure. The sWER calculation method in the Interim Guidance is the site water EC50 divided by the hardness-normalized lab water EC50. In all instances, the Streamlined Procedure sWERs, presented in Table 42, result in lower sWERs compared to sWERs calculated using the Interim Guidance.

Table 43. L.A. River Copper sWERs Summary Calculated Using the Interim Guidance

Sampling Site	sWER				
	Dry Season			Wet Season	
	Event 1	Event 2	Event 3	Event 4	Event 5
T1	12.55	15.14	15.05	---	---
B1	12.99	13.61	13.22	---	---
SDW[1]	7.130	9.370	8.638	---	---
W1	---	---	---	14.15	9.19
LARR	8.184	12.24	8.490	13.37	8.96
LARW	11.69	13.57	10.89	15.29	8.79

--- Dashed line indicates samples were not collected at this site during the event.
1 Simulated downstream water (SDW) created using 7Q10 approach.

7.3 FINAL WATER-EFFECT RATIO CALCULATION

The Streamlined Procedure states that fWERs are calculated as the geometric mean of two (or more) sWERs. The geometric mean is a measure of the central tendency of a data set that minimizes the effects of extreme values and is calculated as the *n*th root of a product of *n* factors. The geometric mean provides a better estimate of the central value of lognormally distributed data than the arithmetic mean. The equation for the geometric mean is:

$$\text{Geometric mean} = \sqrt[n]{y_1 * y_2 * y_3 * ...y_n}$$

As discussed previously, sWERs used to determine the fWERs are calculated per the Streamlined Procedure using the higher of lab-water hardness-normalized EC50 and the hardness-normalized SMAV which yield lower WERs than the Interim Guidance. The Streamlined Procedure calculation methodology is more conservative than the 1994 Interim Guidance methodology because it requires the use of the higher of lab-water EC50 and the SMAV. The following options for calculating scientifically accurate, precise and protective L.A. River copper fWERs using Streamlined Procedure were considered (Table 44):

Option 1: Geometric mean of dry season sWERs by site (Events 1, 2, and 3)
Option 2: Geometric mean of dry weather sWERs by site (Events 1, 2, 3, and 5)
Option 3: Geometric mean of dry season and wet season sWERs by site (Events 1 through 5)
Option 4: Geometric mean of dry weather sWERs for sites with statistically similar sWERs (Events 1, 2, 3, and 5)

The calculation options, presented in Table 44, result in fWERs specific to sites where WER samples were collected. In the case of Option 4, fWERs are specific to sites included in the groupings of statistically similar dry weather sWERs. Section 8 discusses implementation of the recommended fWERs and resulting MCOs to ensure protection of downstream aquatic life beneficial uses intended by the CTR copper criteria.

Table 44. Calculation Options for L.A. River Copper Final WERs (fWERs)[1]

Sampling Site	**Option 1** Geometric Mean of Dry Season sWERs by Site	**Option 2** Geometric Mean of Dry Weather sWERs by Site	**Option 3** Geometric Mean of Dry Season and Wet Season sWERs by Site	**Option 4** Geometric Mean of Dry Weather Statistically Similar sWERs
T1	6.071	6.071	6.071	5.871
B1	5.676	5.676	5.676	
SDW[2]/W1	3.561	3.518	3.661	3.958
LARR	4.052	3.851	3.892	
LARW	5.133	4.577	4.590	

1 Calculated using the Streamlined Procedure.
2 Simulated downstream water (SDW) created using 7Q10 approach.

7.4 RECOMMENDED FINAL COPPER WATER-EFFECT RATIO

Table 45 presents the recommended approach for calculating fWERs during the critical condition (Option 4). fWERs are specific to sites included in the groupings of statistically similar dry weather sWERs. The geometric mean of dry weather statistically similar sWERs (calculated using the SMAV) is the recommended approach as dry weather was identified as the critical condition. Additionally, there are no statistically significant differences between sWERs for T1 and B1 or between SDW/W1, LARR, and LARW. Section 8 discusses the implementation of the recommended fWERs and resulting MCOs to ensure the protection of downstream aquatic life beneficial uses intended by the CTR copper criteria.

Table 45. Recommended Calculation of Final WERs for the L.A. River Copper WER Sampling Sites

Sampling Site	**Option 4** Geometric Mean of Dry Weather Statistically Similar sWERs[1]
T1	5.871
B1	
SDW/W1[2]	3.958
LARR	
LARW	

1 Calculated using the Streamlined Procedure.
2 Simulated downstream water (SDW) created using 7Q10 approach.

7.5 RECOMMENDED SITE SPECIFIC OBJECTIVES

Per the Streamlined Procedures and in accordance with the Interim Guidance, the fWER derived from acute toxicity tests will be applied to both acute and chronic WQC because the fWER derived from acute toxicity tests is expected to be protective of chronic effects. As presented in the Streamlined Procedure and discussed in Allen and Hansen (1996), the fWER derived from acute toxicity tests is expected to be protective of chronic effects “because of the involvement of strong binding agents causes the WER to increase as the effect concentration decreases (USEPA 2001).”

The recommended MCOs are specific to the site(s) where WER toxicity samples were collected. Section 8 discusses the implementation of the recommended fWERs and resulting MCOs to ensure the protection of downstream aquatic life beneficial uses intended by the CTR copper criteria. The recommended MCOs (as dissolved copper) are determined by multiplying the hardness-based CTR freshwater acute and chronic WQC by the fWERs presented in Table 45 as shown in the equations below:

$$MCO_{acute} = CMC = [ACF*\exp(0.9422*\ln(Hardness)+(-1.700))] * fWER$$

$$MCO_{chronic} = CCC = [CCF*\exp(0.8545*\ln(Hardness)+(-1.702))] * fWER$$

Where:

MCOacute = Acute Site Specific Objective [ug/L]
CMC = criterion maximum concentration [ug/L]
ACF = acute conversion factor (0.96)
Hardness [mg/L as CaCO3]
fWER = final water-effect ratio
MCOchronic = Chronic Site Specific Objective [ug/L]
CCC = criterion continuous concentration [ug/L]
CCF = chronic conversion factor (0.96)

The recommended fWERs and MCOs are shown in Table 46.

Table 46. Recommended Dissolved Copper fWERs and MCOs for the L.A. River Copper WER Sampling Sites

Site	Final WER	Acute MCO (ug/L)	Chronic MCO (ug/L)
T1	5.871	[0.96*EXP(0.9422*ln(Hardness)+(-1.700))] * 5.871	[0.96*EXP(0.8545*ln(Hardness)+(-1.702))] * 5. 871
B1			
SDW/W1[1]	3.958	[0.96*EXP(0.9422*ln(Hardness)+(-1.700))] * 3.986	[0.96*EXP(0.8545*ln(Hardness)+(-1.702))] * 3.958
LARR			
LARW			

1 Simulated downstream water (SDW) created using 7Q10 approach.

8 IMPLEMENTATION OF COPPER MCOs

Establishment of MCOs for different sites or reaches of the same waterbody is consistent with state and federal WQC development processes. Waterbodies are often separated into multiple reaches due to varying characteristics. Different WQC are assigned to reaches based on site-specific characteristics. Downstream objectives must be considered when implementing MCOs in NPDES permits and/or total maximum daily loads (TMDLs) to evaluate potential impacts to downstream beneficial uses.

This section presents an evaluation to determine if implementation of the MCOs, presented in Table 46, is protective of downstream aquatic life beneficial uses as intended by the CTR copper WQC. The "protectiveness" of the MCOs was evaluated by comparing existing copper water quality data to the MCOs to determine compliance with the MCOs and whether they would be protective of aquatic life uses as intended by the CTR. Essentially, the analyses simulated the ratio between river copper concentrations and corresponding MCO adjusted criteria. If a ratio exceeded 1.0, the copper concentration exceeded the MCO adjusted criteria and the use is not considered protected as intended by the CTR. Conversely, if the ratio is lower than 1.0, the river is considered protected as intended by the CTR. The following three questions were identified to conduct an evaluation of whether implementation of the MCOs in NPDES permits and/or the L.A. River Metals TMDL is protective of aquatic life uses as intended by the CTR in reaches 1 through 5:

1. Will implementation of the MCO developed for DCTWRP and BWRP (sites T1 and B1, respectively) continue to be protective of aquatic life beneficial uses in Reach 3 above LAGWRP (site SDW/W1) as intended by the CTR copper WQC?
2. Will implementation of MCOs for DCTWRP and BWRP and LAGWRP continue to be protective of aquatic life beneficial uses in Reaches 1 through 3 below the LAGWRP as intended by the CTR copper WQC?
3. Will implementation of the MCO for DCTWRP and BWRP continue to be protective of aquatic life beneficial uses in Reach 4 below DCTWRP as intended by the CTR copper WQC?

From the results of these analyses, it can be determined if the MCOs can be applied to entire reaches of the L.A. River, or to upstream/downstream points relative to the POTWs. Regardless of the results of the evaluation, the MCOs, presented in Table 46, are appropriate because the objectives are based on site-specific characteristics. The approach used to evaluate the protectiveness of the MCOs in reaches downstream from their sample point was to estimate the expected frequency that in-stream dissolved copper concentrations would exceed the MCO in the reach. The methods used to estimate the frequency of exceedance were a combination of Monte-Carlo simulations and mass-balance models. These models were based on the following shared assumptions and characteristics:

- Water quality data were not filtered to exclude wet weather conditions. This increased the variability of the data by incorporating higher copper concentrations and lower hardness associated with wet weather and higher flows. This resulted in an analysis of some conditions that will not occur, but provide a conservative estimation of the potential for low criteria (based on low hardness that only occurs during wet weather conditions) to be present when concentrations are highest, which occurs during low flow conditions.
- The number of days in a three year period was not adjusted to exclude wet weather conditions.
- Dissolved copper concentrations were estimated as the total copper concentration times the

chronic effluent limit translator for LAGWRP or DCTWRP. This assumption is conservative because it overestimates dissolved copper concentration variability in the L.A. River.

- Copper and hardness varied independently (*i.e.*, they were not significantly correlated). The validity of this assumption was confirmed with simple correlation analysis.
- MCO implementation will not result in an increase of copper mass loads from any of the affected POTWs (*i.e.*, the WRPs will maintain the same effective level of treatment in the future). The adoption of MCOs themselves will not result in higher copper loads directly, although an increase in POTW flow and potential copper loads could occur through increased development. However, the TMDL allocation and NPDES permitting process can appropriately address the potential for changes in loads from the POTWs to affect beneficial uses.

A concern was raised that it may not be appropriate to assume that there will be no increase in copper from any of the affected POTWs (or other sources) in the future. River conditions may change over time, post-WER monitoring will continue to provide water quality data that will allow for a reasonable analysis of changing conditions. The analysis presented in this section can be run on a regular basis to evaluate whether River copper conditions are changing and if appropriate actions should be taken through the NPDES and TMDL processes in place. This approach is consistent with EPA and State Board guidance and EPA, State Board, and Regional Board precedent.

Each reach required a slightly different estimation method because equivalent flow and water quality data were not available for each reach. Generally, each Monte-Carlo simulation consisted of estimates for dissolved copper concentrations and the hardness-adjusted MCO for a three-year period (1,095 days) for each reach evaluated. The three-year period was selected to be consistent with the once-in-three-year allowable rate for exceedances of CTR criteria to protect aquatic life. The Monte-Carlo simulation was iterated for 1,000 runs with the results expressed as the ratio of dissolved copper to the hardness-adjusted dissolved copper MCO. The maximum ratio of the simulations (*i.e.*, the highest ratio of dissolved copper to the MCO) was recorded for each three-year iteration. The median of the distribution of three-year maxima is the unbiased best estimate of the maximum ratio of dissolved copper to the MCO expected in a three-year period, and the 2.5th and 97.5th percentiles of the distribution are the 95% confidence limits for the estimate. Specific methods and assumptions used to evaluate the protectiveness for each reach are summarized below.

8.1 WILL IMPLEMENTATION OF THE MCO DEVELOPED FOR SITES T1 AND B1 BE PROTECTIVE OF AQUATIC LIFE BENEFICIAL USES IN REACH 3 ABOVE LAGWRP?

The protectiveness of the MCO immediately below DCTWRP (Reach 4) and BWRP (Burbank Channel) for L.A. River Reach 3 above LAGWRP was evaluated using total copper and hardness data for the L.A. River immediately upstream from LAGWRP. The distributions of total copper and hardness were based on data collected from 1998 through 2005 at the R4 monitoring site upstream of the LAGWRP outfall. Site R4 incorporates all upstream influences on water quality above the LAGWRP outfall. The copper and hardness data were evaluated and determined to be approximately lognormally distributed. The parameters for the distributions were used as inputs for a Monte-Carlo simulation of daily water quality in this section of the L.A. River for a three year period. The simulation incorporated the following conditions and assumptions:

- Water quality measured in Reach 3 above LAGWRP is a reasonable representation of the combined influences affecting Reach 4 below DCTWRP, the Burbank Western Channel below the BWRP, and Verdugo Wash.

- Reach 3 of the L.A. River above LAGWRP during dry weather is primarily a combination of the flows from Reach 4 below DCTWRP and the Burbank Channel below BWRP. Therefore, the WER and resulting MCO for sites T1 and B1 are a reasonable estimate of the effective WER in the L.A. River above LAGWRP.
- Dissolved copper was estimated as the total copper concentration times the effluent limit translator for LAGWRP.

The form of the Monte-Carlo simulation for this reach was:

$$\frac{Tx \cdot Cu_{Total}}{WER \cdot WQO_{Cu,Dissolved}}\text{, which is equal to…}\frac{Tx \cdot Cu_{Total}}{SSO_{Cu,Dissolved}}$$

where,

Tx = translator to convert between total and dissolved copper effluent limits for LAGWRP (0.77),
Cu_{Total} = Random lognormal distribution of total copper in the reach above LAGWRP
WER = the WER for DCTWRP and BWRP (5.9)
$WQO_{Cu,\ dissolved}$ = the CTR chronic criterion for dissolved copper
$MCO_{Cu,\ dissolved}$ = the site-specific CTR chronic criterion for dissolved copper

This equation expands to the following:

$$\frac{0.77 \cdot e^{\phi_{2.568,\ 0.4683}}}{5.9 \cdot 0.96 \cdot e^{(0.8545 \cdot \phi_{5.534,\ 0.2530}) - 1.702}}$$

8.1.1.1 Results for Analysis for Reach 3 Upstream of LAGWRP

Based on the Monte-Carlo simulation results, the expected maximum ratio of dissolved copper in the L.A. River immediately upstream of LAGWRP to the hardness-adjusted MCO in a three-year period is 0.452, with 95% confidence limits of 0.349 – 0.723. This means that dissolved copper concentrations would not exceed the MCO more than once in a three year period. In fact, the unbiased estimate (the median) of the highest dissolved copper concentration in this reach during a three-year period is expected to be less than half of the hardness-adjusted MCO. This result indicates that implementing the MCO based on a WER of 5.9 and resulting MCO for sites T1 and B1 will be protective of Reach 3 aquatic life beneficial uses of the L.A. River above LAGWRP as intended by the CTR copper WQC. The results of the Monte-Carlo simulations are presented in Figure 15.

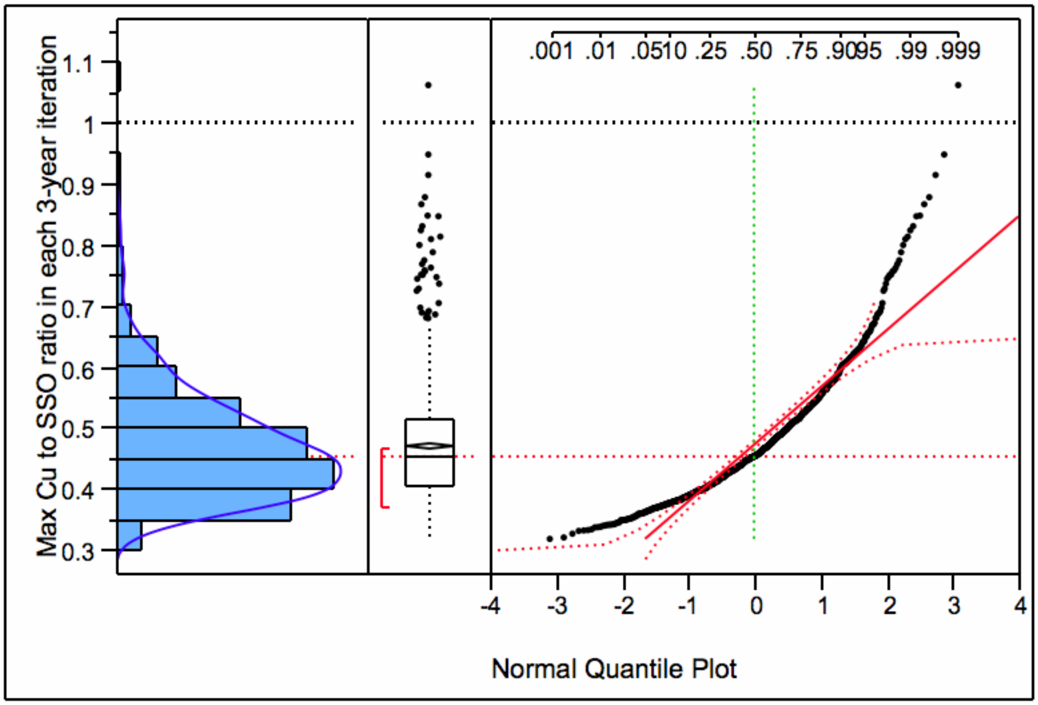


Figure 15. Distribution of the Results of Monte-Carlo simulations for L.A. River in Reach 3 Above LAGWRP and Below the Confluence of Reach 4 and Burbank Western Channel

Note: Distribution of the maximum ratio of dissolved copper to MCO expected in a three year period from 1,000 model iterations. The y-axis is the ratio of dissolved copper to MCO. A dotted horizontal line at 1.0 indicates the ratio representing an exceedance of the MCO. Each point is the maximum ratio from one three-year simulation, and the median of the distribution of results represents the expected or typical maximum for a three-year period.

8.2 WILL IMPLEMENTATION OF THE MCO DEVELOPED FOR SITES T1, B1, AND SDW/W1 BE PROTECTIVE OF AQUATIC LIFE BENEFICIAL USES IN REACHES 1 THROUGH 3 BELOW THE LAGWRP?

The protectiveness of the MCO for LAGWRP for L.A. River reaches below LAGWRP (Reaches 1-3) was evaluated in a simplified mass balance model using total copper and hardness data for the L.A. River immediately upstream of LAGWRP and LAGWRP effluent quality. The distributions of total copper and hardness were based on data collected from 1998 through 2005 at the R4 monitoring site upstream from the LAGWRP outfall. This site incorporates all upstream influences on water quality above the LAGWRP outfall. LAGWRP effluent quality was modeled using data collected from 1998 through 2004. Because there are no flow data readily available upstream of LAGWRP, the flow balance element of the model was initially based on the distribution of the ratio of LAGWRP effluent to downstream L.A. River flows above the Arroyo Seco Channel (LARA). Copper and hardness data were evaluated and determined to be approximately lognormally distributed. The parameters for the distributions were the inputs for a Monte-

Carlo simulation of daily water quality in this section of the L.A. River for a three year period. This simulation incorporated the following conditions and assumptions:

- Water quality measured in Reach 3 above LAGWRP is a reasonable representation of the combined upstream influences affecting Reach 3, including the DCTWRP, the Burbank Channel below BWRP, and Verdugo Wash. Water quality in this reach is not expected to change as a result of implementation of the MCO.
- The initial evaluation model was simplified to the maximum ratio of effluent to downstream flows at LARA. This was a conservative assessment of the potential impact of LAGWRP effluent because the proportion of effluent flows is reduced by flows from the Arroyo Seco Channel, Rio Hondo, and Compton Creek in Reach 2 and Reach 1 below LARA. The distribution of the proportion of effluent in L.A. River flows at LARA was based on LAGWRP and LARA flow data for August 2005 through August 2006. This distribution in presented in Figure 16 and Table 47.

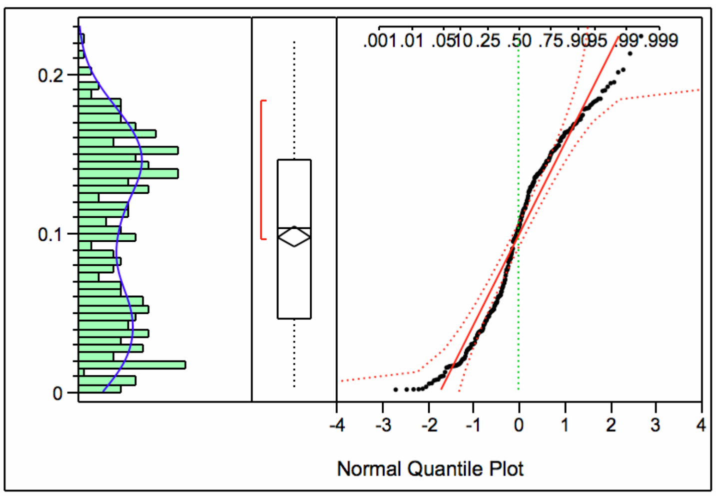


Figure 16. Distribution of the proportion of LAGWRP effluent in the L.A. River above the Arroyo Seco Channel, August 2005 to August 2006.
Note: The y-axis is the ratio of LAGWRP effluent to river flows measured at LARA.

Table 47. Quantiles of the Distribution of Proportion of LAGWRP Effluent in the L.A. River above the Arroyo Seco Channel, August 2005 to August 2006.

Quantile	LAGWRP Effluent Proportion
99.5%	0.21922
97.5%	0.19181
90.0%	0.16941
75.0%	0.14638
50.0%	0.10288
25.0%	0.04686
10.0%	0.01784
2.5%	0.00491
0.5%	0.00132

The form of the Monte-Carlo simulation for this reach was:

$$\frac{Tx \cdot (DS\ Cu_{Total})}{WER \cdot DS\ WQO_{Cu\ Dissolved}}$$

where,

Tx = translator to convert between total and dissolved copper effluent limits for LAGWRP (0.77),
WER = the WER for Reach 1-3 below LAGWRP (4.0),
DS Cu_{Total} = Total copper in Reach 3 below LAGWRP, and

$$DS\ Cu_{Total} = 0.25 \cdot LAG\ Cu_{Total} + 0.75 \cdot R4\ Cu_{Total}$$

where,

LAG Cu_{Total} and *R4* Cu_{Total} are the random lognormal distributions of total copper in LAGWRP effluent and in Reach 3 above LAGWRP, respectively, and

DS $WQO_{Cu,\ dissolved}$ = the hardness-adjusted CTR chronic criterion for dissolved copper in Reach 3 below LAGWRP. This is based on downstream hardness modeled similarly to total copper,

$$DS\ Hardness = 0.25 \cdot LAG\ Hardness + 0.75 \cdot R4\ Hardness$$

where,

LAG Hardness and *R4 Hardness* are the random lognormal distributions of hardness in LAGWRP effluent and in Reach 3 above LAGWRP, respectively.

This equation expands to:

$$\frac{0.77 \cdot \left(0.25 \cdot e^{\phi_{2.361,\ 0.4025}} + 0.75 \cdot e^{\phi_{2.568,\ 0.4683}}\right)}{4.0 \cdot 0.96 \cdot e^{\left(0.8545 \cdot \ln\left(0.25 \cdot e^{\phi_{5.454,\ 0.253}} + 0.75 \cdot e^{\phi_{5.534,\ 0.1013}}\right) - 1.702\right)}}$$

8.2.1.1 Results for Analysis for Reaches Downstream of LAGWRP

Based on Monte-Carlo simulation results, the expected maximum ratio of dissolved copper in the L.A. River immediately downstream of the LAGWRP to the hardness-adjusted MCO in a three year period is 0.509, with 95% confidence limits of 0.391 – 0.763. The results are summarized in Figure 17. This means that dissolved copper concentrations would not exceed the MCO more than once in a three year period. The unbiased estimate of the highest dissolved copper concentration expected in Reaches 1 through 3 downstream of LAGWRP during a three-year period (the median of the distribution) is expected to be approximately half of the hardness-adjusted MCO. This result indicates that implementing the MCOs based on a WER of 4.0 for the reaches below LAGWRP and a WER of 5.9 for the reaches below the DCTWRP and BWRP will be protective of aquatic life beneficial uses of the L.A. River in Reaches 1 through 3 as intended by the CTR copper WQC. A separate analysis was conducted using the default translator value of 0.96. Based on Monte-Carlo simulation results with the default translator of 0.96, the expected maximum ratio of dissolved copper in the L.A. River immediately downstream of the LAGWRP to the hardness-adjusted MCO in a three year period is 0.644, with 95% confidence limits of 0.490 – 0.941. Although the default translator is conservative in that it overestimates the proportion of dissolved copper in the LA River, this result further supports the initial conclusion reached using the site-specific translator of 0.77.

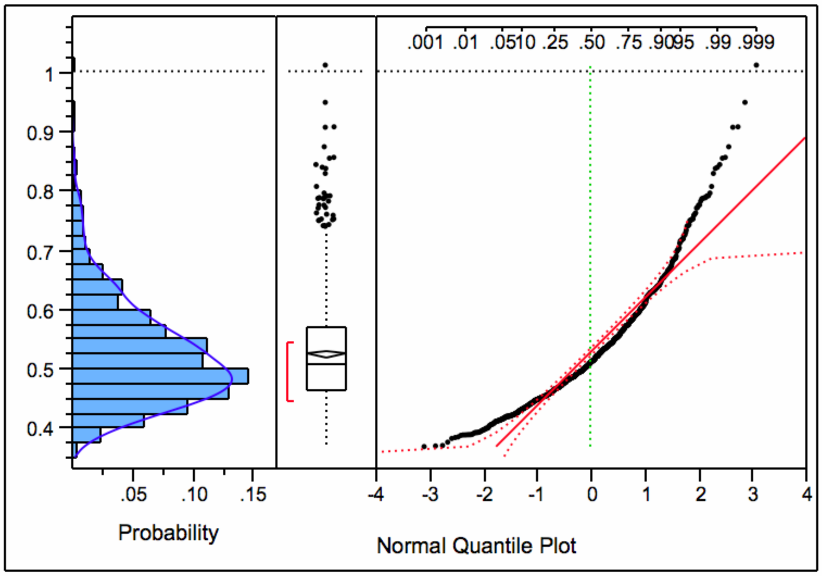


Figure 17. Distribution of the results of Monte-Carlo simulations for L.A. River in Reach 3 below LAGWRP.

Note: Distribution of maximum ratio of dissolved copper to MCO expected in a three-year period from 1,000 model iterations. The y-axis is the ratio of dissolved copper to MCO. A dotted horizontal line at 1.0 indicates the ratio representing an exceedance of the MCO. Each point is the maximum ratio from one three-year simulation, and the median of the distribution of results represents the expected or typical maximum for a three-year period.

8.3 WILL IMPLEMENTATION OF THE MCO DEVELOPED FOR SITES T1 AND B1 BE PROTECTIVE OF AQUATIC LIFE BENEFICIAL USES IN REACH 4 BELOW THE DCTWRP?

The protectiveness of the MCO immediately below DCTWRP (Reach 4) was evaluated based on the analyses presented above, and a previous analysis of critical conditions for this Study (*LA River Critical Sampling Conditions for Cu WER Studies*, August 14, 2005 contained in Appendix 11). This approach was required because there were no available water quality data for Reach 4 below the DCTWRP discharge. Factors influencing the water quality in this reach include flows upstream of DCTWRP, Tujunga Wash flows, urban runoff, and groundwater. However, dry weather flows in this reach are dominated by DCTWRP effluent flows. Flow data for DCTWRP and the L.A. River below Tujunga Wash (LART) were evaluated for January 2004 through April 2007. Based on these recent flow data, DCTWRP effluent flows account for at least 50% of the flows in this reach approximately 75% of the time (Figure 18). The bimodal nature of the distribution is due to wet weather high flows that result in the low proportion of DCTWRP flows at LART. The MCOs for DCTWRP and BWRP are based on WERs in 100% effluent because there is little or no diluting flow in the L.A. River below these discharges during dry weather.

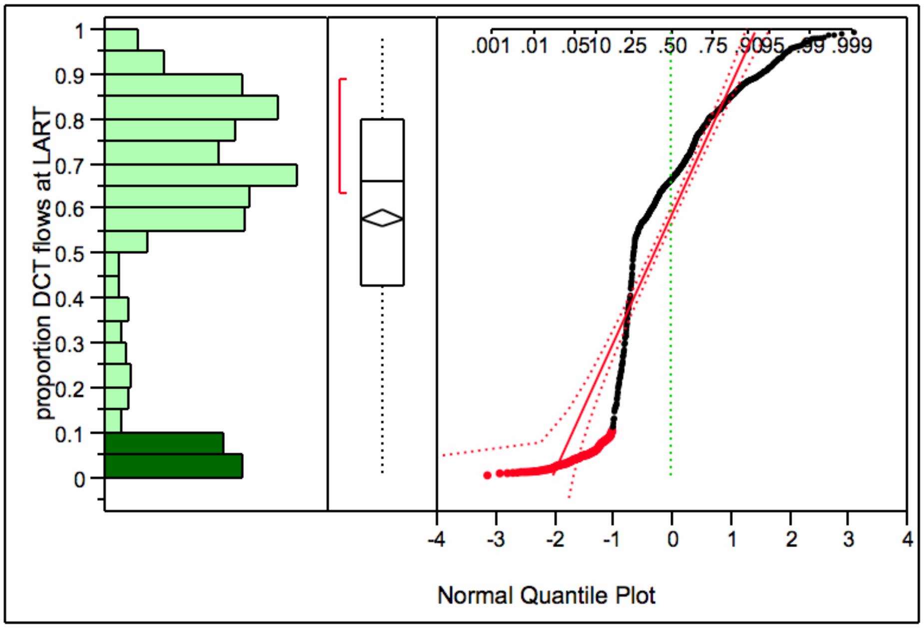


Figure 18. Cumulative Distribution Function Plot: Proportion of Tillman WRP Discharge at LART
Note: The bimodal distribution evident in the proportion of DCTWRP effluent at LART is due to wet weather high flow events (highlighted in the quantile plot as red points) that result in a low proportion of DCTWRP flow at LART.

To summarize, the following factors were considered in assessing whether MCO implementation for the DCTWRP and BWRP are protective of Reach 4 below the DCTWRP outfall:

- The MCO based on the WER for DCTWRP and BWRP is by definition protective of DCTWRP discharges.
- DCTWRP discharges are the dominant component of dry weather flows in Reach 4.
- WERs have been demonstrated by this Study to be similar or higher during storm flows.
- Other sources of flows in Reach 4 (primarily dry weather urban runoff, groundwater, and upstream flows) are not reasonably expected to significantly reduce the WER in Reach 4.
- The analysis presented in the August 14, 2005 memorandum established that dry season dry weather conditions are the critical conditions for this Study (*i.e.*, a WER based on dry season, dry weather conditions would be protective for storm flows and dry weather conditions in wet season). In other words, conditions when Reach 4 is not dominated by DCTWRP discharges would not result in less protectiveness.
- An MCO based on a WER of 5.9 was determined to be protective for Reach 3 above LAGWRP, based on measured water quality data in this reach. Dry weather flows in this reach are primarily Reach 4 flows and BWRP effluent.

The only component of Reach 4 not explicitly characterized by this Study is bracketed by the DCTWRP and Reach 3 below the confluence of Reach 4 and Burbank Channel. An MCO based on a WER of 5.9 was determined to be protective in both these bracketing reaches, which also supported the uncharacterized components of Reach 4 below DCTWRP. This is illustrated in Figure 19.

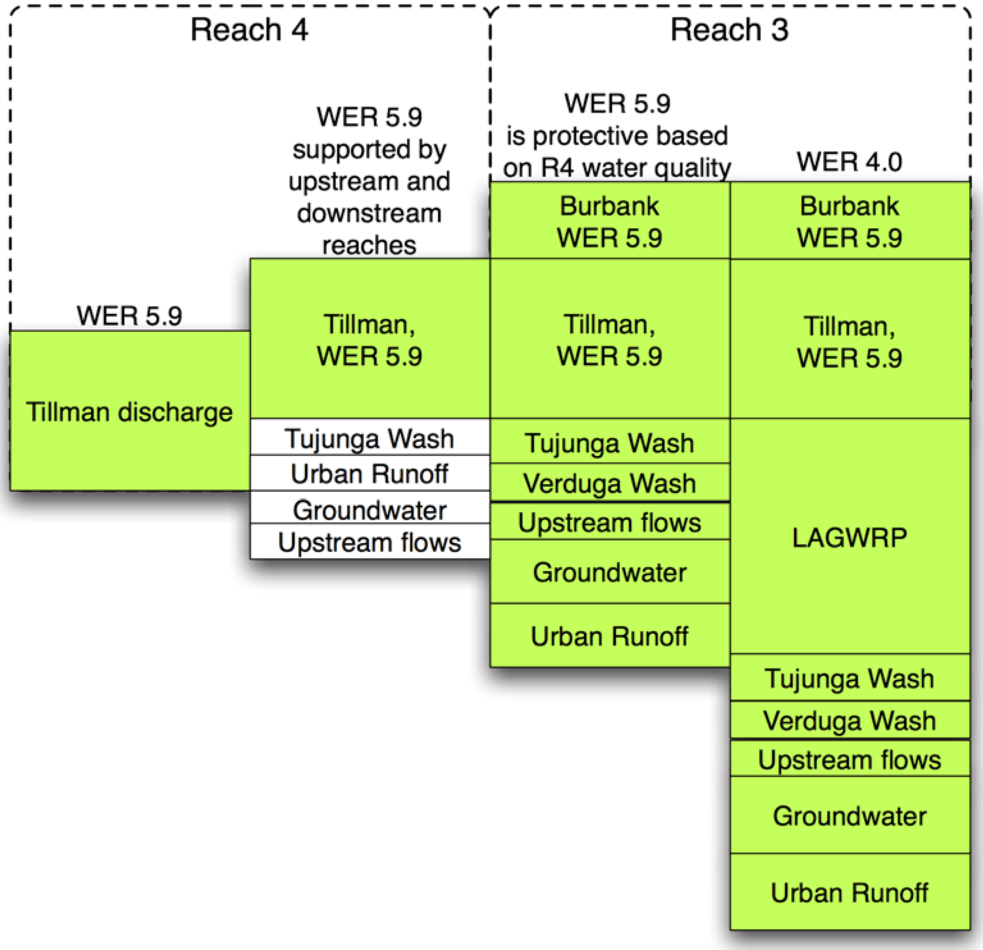


Figure 19. Flow Components of Reach 3 and Reach 4

Note: Shaded elements are explicitly characterized by the WER study or determined by direct evaluation of available water quality data for ability to comply with MCOs.

8.4 RECOMMENDED IMPLEMENTATION OF COPPER MCOs

Establishment of MCOs for different sites or reaches in the same waterbody is consistent with state and federal WQC development processes. The analysis presented above evaluated whether implementation of the MCOs presented in Table 46 are protective of downstream aquatic life beneficial uses as intended by the CTR copper WQC. The approach used to evaluate the protectiveness of the MCOs in reaches downstream from their application was estimating the expected frequency that in-stream dissolved copper concentrations would exceed the MCO in the reach. The methods used to estimate the frequency of exceedance were a combination of Monte-Carlo simulations and mass-balance models.

The results of the analysis are presented graphically in Figure 20 and in the following summary:

- MCO application based on a WER of 5.9 for DCTWRP and BWRP (sites T1 and B1, respectively) to Reach 3 upstream of LAGWRP will be protective of aquatic life beneficial uses in this portion of Reach 3 as intended by the CTR copper WQC.
- MCO application based on a WER of 5.9 for DCTWRP and BWRP (sites T1 and B1, respectively) to Reach 3 upstream of the LAGWRP (site SDW/W1) and MCO application based on a WER of 4.0 downstream of LAGWRP will be protective of aquatic life beneficial uses of Reaches 3 through 1 as intended by the CTR copper WQC.
- MCO application based on a WER of 5.9 for DCTWRP and BWRP (sites T1 and B1, respectively) to Reach 4 downstream of the DCTWRP will be protective of aquatic life beneficial uses in this portion of Reach 3 as intended by the CTR copper WQC.

Based on these findings, Table 48 presents the final recommended WERs and MCOs for each reach of the L.A. River evaluated through this Study. Table 49 presents the CMC and CCC based on the final recommended WERs and MCOs at various hardness values.

Table 48. Recommended Dissolved Copper fWERs and MCOs for the L.A. River Copper WER Sampling Sites

Site	Applicable Reaches Associated with fWER and MCO	Final WER	Acute MCO (ug/L)	Chronic MCO (ug/L)
T1 B1	L.A. River Reach 3 upstream of LAGWRP, L.A. River Reach 4, and Burbank Western Channel	5.871	[0.96*EXP(0.9422*ln(Hardness)+(-1.700))] * 5.871	[0.96*EXP(0.8545*ln(Hardness)+(-1.702))] * 5.871
SDW / W1 LARR LARW	L.A. River Reach 3 downstream of LAGWRP and L.A. River Reaches 1 and 2	3.958	[0.96*EXP(0.9422*ln(Hardness)+(-1.700))] * 3.958	[0.96*EXP(0.8545*ln(Hardness)+(-1.702))] * 3.958

1 Simulated downstream water (SDW) created using 7Q10 approach.

Table 49. Dissolved Copper CMC and CCC Values Based on Recommend MCOs at Hardness of 50, 100, and 200 mg/L ($CaCO_3$)

Site	Applicable Reaches Associated with fWER and MCO	CMC and CCC at Hardness of 50 mg/L ($CaCO_3$) (ug/L)		CMC and CCC at Hardness of 100 mg/L ($CaCO_3$) (ug/L)		CMC and CCC at Hardness of 200 mg/L ($CaCO_3$) (ug/L)	
		CMC	CCC	CMC	CCC	CMC	CCC
T1 B1	L.A. River Reach 3 upstream of LAGWRP, L.A. River Reach 4, and Burbank Western Channel	41.1	29.1	78.9	52.6	152	95.1
SDW / W1[1] LARR LARW	L.A. River Reach 3 downstream of LAGWRP and L.A. River Reaches 1 and 2	27.9	19.7	53.6	35.7	103	64.5

1 Simulated downstream water (SDW) created using 7Q10 approach.

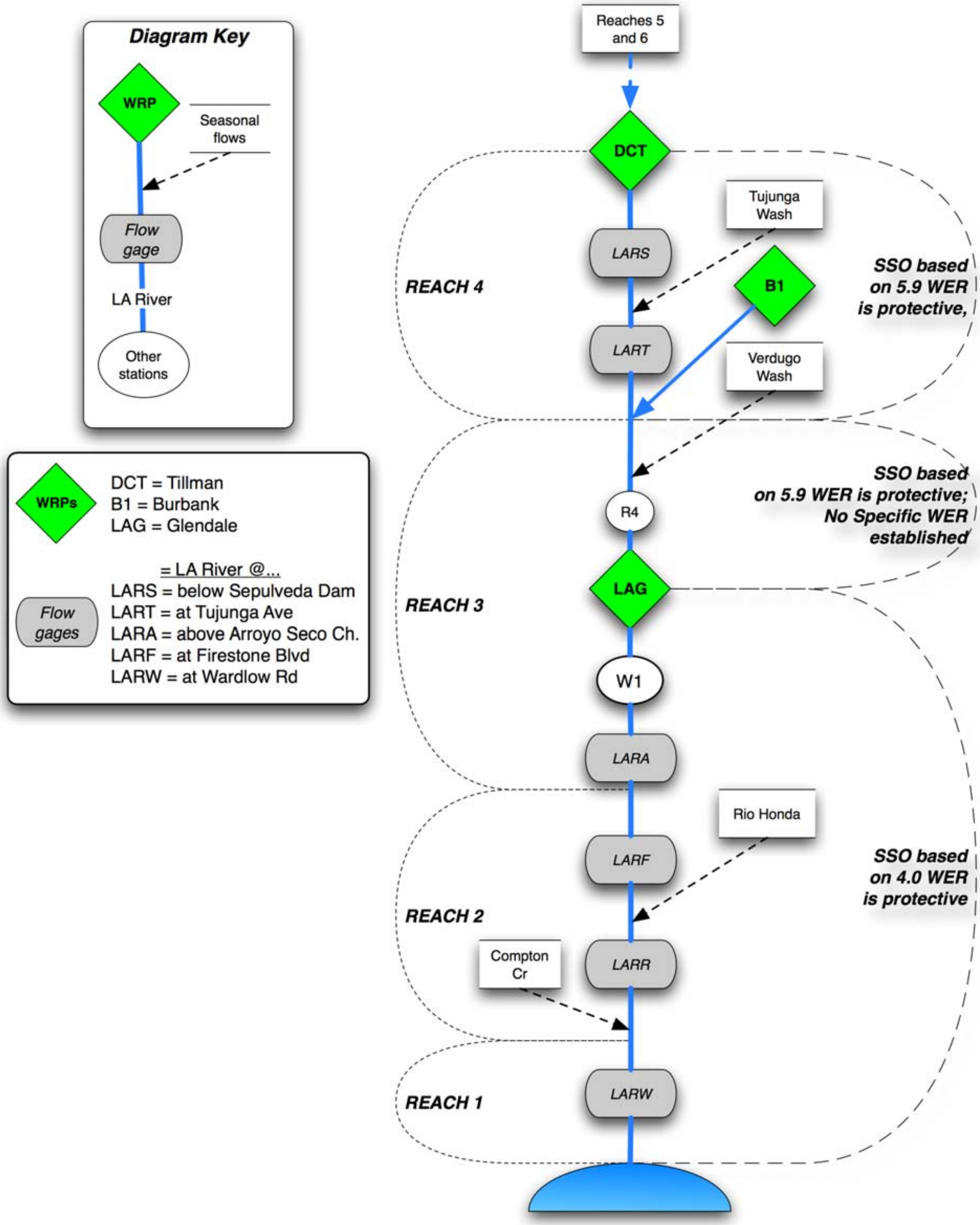


Figure 20. Summary of MCO Implementation and Protectiveness for L.A. River Reaches 1 – 4

9 BIOTIC LIGAND MODEL ANALYSIS

The BLM is a software program created by HydroQual Inc. to evaluate bioavailability and toxicity of metals that have been discharged into surface water. The model considers several water quality parameters, including hardness, DOC, chloride, pH, and alkalinity. The BLM predicts speciation and toxicity of trace metals to aquatic organisms based on concentrations of complexing compounds (*e.g.*, DOC) and competing cations.

USEPA released the February 2007 Copper Criteria Document, which utilizes the BLM to calculate copper WQC in freshwater. The Copper Criteria Document is intended to provide states with guidance in establishing water quality standards and does not constitute a regulation. The Copper Criteria Document utilizes the BLM version 2.2.3 (March 2007) to develop copper WQC. If the BLM appropriately characterizes copper toxicity in the L.A. River, complexing compound data collected from L.A. River samples may be used in the future to predict copper toxicity to aquatic life.

Water quality parameters required as inputs to the BLM were collected as part of this Study to provide useful data to BLM researchers and to ensure the data set collected for the L.A. River can be used in the BLM at a later date. BLM analyses were conducted for the following:

- Evaluate the ability of the BLM to predict copper EC50 in comparison with toxicity tests.
- Evaluate the ability of the BLM to predict copper WQC in comparison with the toxicity tests-based WERs and hardness-based equation.

Appendix 13 presents the aforementioned evaluations, as well as the input parameters used, and a sensitivity analysis on several BLM input parameters such as pH, DOC, and humic acid.

The following is a brief summary of the analysis and conclusions presented in Appendix 13. The current version of the BLM does not produce EC50 results for *C. dubia* when used to simulate copper toxicity. BLM Version 2.1.2 (June 2005) is the most recent version that provides EC50 results and was used for the analysis described here. Per a conversation with HydroQual on June 1, 2007, BLM results between Versions 2.1.2 and 2.2.3 (most recent) vary by no more than 10% (Robert Santore, HydroQual, pers. Comm., June 1, 2007).

BLM results were compared to toxicity test results for effluent, L.A. River and lab water samples. Several variations of the input parameters measured during this Study were also evaluated to assess the most appropriate BLM input parameters for the L.A. River. As discussed more fully in Appendix 13 these calibrations and simulations resulted in the following conclusions:

- For the L.A. River, the BLM generally predicted EC50s that were on average twice as high (up to four times higher) than the observed EC50s. The Copper Criteria Document predicted criteria results that deviated from criteria generated based on observed toxicity tests by a factor of 1.3 on average to slightly more than 2. Further, HydroQual confirmed the deviation was within the range (slope of ½ to 2) of typical data that were modeled using the BLM during development (Robert Santore, HydroQual, pers. Comm., June 1, 2007).

- The BLM appeared to predict Streamlined Procedure sWERs-based copper CMCs better than Interim Guidance sWERs-based copper CMCs for the L.A. River and effluent sites.
- The BLM estimated less stringent copper CMCs for the Los Angeles River sites when compared to the hardness-based copper CMCs using Streamlined Procedure sWERs in 10 of 12 instances.
- The BLM typically estimated more stringent copper CMCs for the effluent sites when compared to the hardness-based copper criteria using sWERs determined with the Streamlined Procedure (five of six instances).
- The BLM did not appear to accurately predict copper WQC or EC50s for effluent sites.
- From the sensitivity analyses presented in Attachment 1 of Appendix 13, , the pH recorded immediately upon receipt at the lab (or designated as pH original) is an appropriate BLM input for L.A. River sites, and is the most practical input for future BLM uses.
- From the sensitivity analyses presented in Attachment 1 of Appendix 13, higher humic acid concentrations appear to reduce the low bias when comparing BLM results to hardness-based calculated copper CMCs using an Interim Guidance WER. It may be worthwhile to analyze for humic acid in the Los Angeles River to validate the assumed 10% concentration used in this analysis.
- From the sensitivity analyses presented in Attachment 1 of Appendix 13, DOC data that were qualified as biased due to possible contamination may have decreased the accuracy of the slope by approximately 10%.

USEPA does not currently provide guidance on how to develop a single copper water quality criterion based on the BLM at this time as BLM criterion calculations are event- and/or time-variable. Additional study is necessary to evaluate the use of the BLM in various scenarios as well as methods for calculating a single copper criterion that is not event- and/or time-variable.

The BLM analysis conducted for the L.A. River Cu WER Study are only a part of the ongoing effort to further refine the use and evaluate the applicability of the BLM. Based on the study results the BLM continues to be a potentially viable approach to evaluating site-specific criteria for copper in the L.A. River.

10 KEY COMMENTS/CONCERNS IDENTIFIED DURING WORK PLAN DEVELOPMENT

An iterative process was used in developing the L.A. River Copper WER Study. Various stakeholders (including RWQCB and USEPA) as well as the TAC participated in review and comment on several versions of the Work Plan. Those comments resulted in additional testing to confirm assumptions as well as answered questions not addressed in the original Work Plan and increased confidence in the determination of scientifically accurate, precise and protective copper WERs for the L.A. River. The key comments/concerns that drove added testing included:

1. Do concentrations of target chemical parameters vary over the 24-hour composite period?
2. Is dry weather the critical condition?
3. Are WERs for downstream segments of the L.A. River lower or higher than the segments the POTWs discharge to?

Although the results of the additional testing are presented throughout this report, the following sections are included to briefly summarize the additional testing and results which address the key comments/concerns.

10.1 ADDITIONAL TESTING TO ASSESS VARIABILITY

As discussed in Section 6.1 (Variability Analysis), a variability analysis was conducted to evaluate if significant changes occurred with regard to concentrations of chemical parameters over the duration of a 24-hour composite collection. The variability analysis results did not indicate a significant difference between samples analyzed immediately upon receipt or 24 hours after receipt, except for DO. This suggests that using composite samples for the study would appropriately represent in-stream conditions and result in a representative WER.

10.2 ADDITIONAL TESTING TO CONFIRM CRITICAL CONDITION

A primary assumption of the first Work Plan was that dry weather represented the critical condition. This assumption was supported by an analysis using the BLM [See Appendix B of the Final Work Plan (LWA 2005)]. However, to confirm the assumption additional testing was conducted, which included:

1. Wet season wet weather WER testing
2. Wet season dry weather WER testing
3. Evaluation of chemical parameters during a “shoulder event”

Wet season wet weather WER testing results, which are presented in Section 6, indicate wet season wet weather WERs were higher than dry weather WERs. Additionally, copper concentrations were lower and flows were higher in wet weather resulting in higher assimilative capacity during these conditions. Wet season dry weather WER testing results, also presented in Section 6, indicate that wet season dry weather sWERs were not statistically different from dry season dry weather sWERs and were combined with the dry season dry weather sWERs in fWER calculations. Evaluation of chemical parameters collected during a “shoulder event”, presented in Section 6.2, confirmed assumptions presented in the memorandums evaluating these conditions (Appendix 11), which indicated the “shoulder event” do not represent a critical condition.

Overall, the results of additional WER and chemical analysis confirmed the primary assumption that dry weather was the critical condition for determination of a copper WER.

10.3 ADDITIONAL TESTING TO EVALUATE DOWNSTREAM CONDITIONS

The initial scope of this Study was limited to the L.A. River reaches into which the three POTWs discharge. However, concern was raised about potential implications to downstream reaches and whether downstream WERs were different than segments into which the POTWs discharge. To address these concerns, the scope of this Study was expanded to add two downstream sampling sites in the lower freshwater reach of the L.A. River

The results of WER testing completed for all sites, including the two downstream sampling sites (LARR and LARW) are presented in Section 6. The results indicate that WERs at the downstream sampling sites are in the range of WERs for the three upstream sites. The addition of two downstream sites to this Study allowed for development of WERs specific to each reach.

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