Chollas Creek
Copper, Lead, and Zinc
Water-Effect Ratio Study

Final Report
May 27, 2011

City of San Diego

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Copper, Lead, and Zinc
Water-Effect Ratio Study

Final Report

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ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
BLM	Biotic Ligand Model
BMP	Best Management Practice
CCC	Criteria Continuous Concentration
CMC	Criteria Maximum Concentration
COC	chain-of-custody
CRG	CRG Marine Laboratories, Inc.
CRM	Certified reference material
CTR	California Toxics Rule
CWA	Clean Water Act
DO	dissolved oxygen
DOC	dissolved organic carbon
DMW	dilute mineral water
FACR	Final Acute–Chronic Ratio
FAV	Final Acute Value
GC-MS	gas chromatography-mass spectrometry
GMAV	Genus Mean Acute Value
HDPE	high density polyethylene
ICP-MS	inductively coupled plasma-mass spectrometry
LC_{50}	median lethal concentration
LDPE	low density polyethylene
LWA	Larry Walker Associates
MLS	mass loading station
MS4	Municipal Separate Storm Sewer System
NCI	negative chemical ionization
NEXRAD	Next Generation Radar
PAH	polycyclic aromatic hydrocarbon
PBO	piperonyl butoxide
PCB	polychlorinated biphenyl
Port	Port of San Diego
POTW	publically owned treatment works
pH	hydrogen ion concentration
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
QPF	quantitative precipitation forecast
Regional Board	California Regional Water Quality Control Board, San Diego Region
RPD	relative percent difference
SMACR	Species Mean Acute–Chronic Ratio
SM	Standard Methods
SMAV	Species Mean Acute Value
SMACR	Species Mean Acute–Chronic Ratio
SOPs	Standard Operating Procedures
SRM	Standard Reference Material
SSO	site specific objective
TAC	technical advisory committee

ACRONYMS AND ABBREVIATIONS (Continued)

TDS	total dissolved solids
TIE	toxicity identification evaluation
TMDL	Total Maximum Daily Load
TOC	total organic carbon
TSS	total suspended solids
USEPA	United States Environmental Protection Agency
WER	water-effect ratio
WESTON	Weston Solutions, Inc.
WGS 84	World Geodetic System 1984
WLA	waste load allocation
WQO	water quality objective

UNITS OF MEASURE

cfs	cubic feet per second
°C	degrees Celsius
Ft	feet or foot
L	liter
µg/L	microgram per liter
mg/L	milligram per liter
mL	milliliter
ng/L	nanogram per liter
ppb	parts per billion

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EXECUTIVE SUMMARY

This report presents the results of the *Chollas Creek Copper, Lead, and Zinc Water-Effect Ratio (WER) Study*. This study was conducted to develop site-specific water quality objectives (WQOs) for Chollas Creek in accordance with the California Toxics Rule (CTR) for dissolved metals. The CTR was used for the basis of the Chollas Creek Dissolved Copper, Lead, and Zinc Total Maximum Daily Load (TMDL), which incorporated a provision for developing site-specific objectives (SSOs). The development of SSOs is applicable when criteria are either over- or under-protective of the beneficial uses. In the case of Chollas Creek, the current hardness-based CTR criteria were identified as overprotective. The SSO is a scientifically developed WQO that takes into account all chemical factors present (e.g., total organic carbon, alkalinity, sulfate, and pH), as opposed to just hardness, to assess the true bioavailability of a given metal (USEPA, 1994, 1997).

WER studies can result in more or less protective criteria depending on site-specific conditions of the given waterbody. The United States Environmental Protection Agency (USEPA) recommends a WER procedure (i.e., a criteria adjustment factor accounting for the effect of site-specific water characteristics on pollutant bioavailability and toxicity to aquatic life) for determining site-specific values in the 1994 *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (EPA-823-B-94-001). Specifically, use of the WER Procedure is to account for any difference that exists between the toxicity of a pollutant in laboratory dilution water and its toxicity in site water (USEPA, 1994; Regional Board, 2007).

The CTR WQO equations are currently based on the inverse relationship between hardness and toxicity. The CTR lists a criteria maximum concentration (CMC) (i.e., acute criteria) and criteria continuous concentration (CCC) (i.e., chronic criteria) calculated using hardness concentrations from each sampling event to determine the WQOs for each dissolved metal (Regional Board, 2007):

> **CCC = (WER) * (*CFC*) * {*e*^[(*mC* * *ln* hardnes*s*) + *bC*]}**
>
> where: *CFC* = conversion factor for freshwater chronic criteria
>   *e*   = mathematical constant
>   *mC*   = slope factor for chronic criteria
>   *ln*   = natural log
>   *bC*   = y intercept for chronic criteria

The default value of 1 (most conservative) is used when an SSO has not been determined.

> **CMC = (WER) * (*CFA*) * {*e*^[(*mA* * *ln* hardness) + *bA*]}**
>
> where: *CFA* = conversion factor for freshwater acute criteria
>   *e*   = mathematical constant
>   *mA*   = slope factor for acute criteria
>   *ln*   = natural log
>   *bA*   = y intercept for acute criteria

The WER is a variable of the CCC and CMC equations, which can be used to develop an SSO, where the following applies:

$$WER = \frac{LC_{50} \text{ site water}}{LC_{50} \text{ laboratory water}}$$

LC_{50} = median lethal concentration

Upon completion of a final WER (i.e., geometric mean of three or more representative WER events) and submission to the California Regional Water Quality Control Board (Regional Board), determination of the SSOs can then be calculated by substituting the final WER value into the CCC and CMC equations for the calculation of site-specific criteria (Regional Board, 2007).

While it was relevant to apply a WER in the case of Chollas Creek, the Regional Board indicated it was the responsibility of the named dischargers to develop the WER and SSO, if determined feasible. In the case of Chollas Creek, the potential cost of treatment Best Management Practices (BMP) were estimated to be significant to comply with the existing water quality criteria, thus it was determined by the dischargers that investigation of a WER(s) and SSO(s) were necessary as an integral step in assessing compliance during TMDL implementation.

The objective of this study was to establish WERs and SSOs for dissolved copper, lead, and zinc, separately for Chollas Creek. The Chollas Creek WER study was conducted in accordance with the *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (USEPA, 1994). Sampling sites were located near the mouth of the north fork of Chollas Creek (SD8(1)) and near the mouth of the south fork of Chollas Creek (DPR2). The two sites are located at the TMDL compliance monitoring stations (Figure 4-1). An additional program objective was to determine whether these two sites demonstrate statistically different WERs and whether or not a single WER and SSO can be applied to the whole watershed.

The results of the WER study are presented in Table ES-1 for dissolved copper and dissolved zinc.

Table ES-1. Final Dissolved Copper and Zinc Water-Effect Ratios for SD8(1)-North Fork and DPR2-South Fork of Chollas Creek (geometric mean)

Station	Copper WER	Zinc WER
SD8(1)-North Fork (n=5)	4.64	1.40
DPR2-South Fork (n=4)	5.56	1.60

Lead WERs were not pursued due to the insolubility of lead in neutral waters, such as are found in Chollas Creek. Lead solubility curves indicate that significant lowering of hydrogen ion concentration (pH) would be required to solubilize the lead in laboratory test solutions. Because the test organisms were more sensitive to low pH, the tests were not representative of typical site conditions and were terminated. During this evaluation, it was discovered that USEPA was in the process of revising the aquatic lead criteria. Similar situations had been brought to USEPA's attention in which acid soluble tests (i.e., not representative) were included in original criteria development, which subsequently resulted in overprotective criteria. Based on recently available

USEPA aquatic toxicity results, a new freshwater CMC for dissolved lead (µg/L) is being developed.

- In the interim, the recently available USEPA lead toxicity curves were used to calculate a freshwater Final Acute Value (FAV) for total lead at a hardness of 50 mg/L to be 95.96 µg/L. The total lead FAV was converted using the conversion factor (CF) 0.892 to a new dissolved lead FAV of 85.60 µg/L.

- A new freshwater CMC for dissolved lead (µg/L) was developed as follows:

$$e^{(1.442[ln(\textbf{hardness})]-1.884)}$$

  where: e = constant

  ln = natural log

- A new freshwater CCC for dissolved lead (µg/L) was developed as follows:

$$e^{(1.442[ln(\textbf{hardness})]-3.421)}$$

  where: e = constant

  ln = natural log

Evaluation of Results

- Based on the study data collected to date, historical compliance results for both sites were re-evaluated to compare the number of exceedances from existing criteria to the new site-specific criteria. Results showed that exceedances were greatly reduced when incorporating the newly developed WERs and that the current hardness-based TMDL criteria are overprotective.

- Based on the re-calculation and comparison to historical results, there were no exceedances in the South Fork site DPR2 for any metal. In the North Fork, there were two exceedances of dissolved copper, nine dissolved zinc exceedances, and three exceedances of dissolved lead.

- Toxicity test results also provide another line of evidence supporting the WER results, which indicate that toxicity to *Ceriodaphnia dubia* is no longer a persistent issue as a result of the USEPA ban on the pesticide Diazinon in 2005 (suggesting metals were not a significant factor in the observed toxicity).

Biotic Ligand Model

The biotic ligand model (BLM) is a conceptual framework for estimating effects of metals to aquatic organisms (Di Toro et al., 2001; Santore et al., 2001). This framework has been utilized to develop predictive toxicity models for a number of organisms and a number of metals, including copper, lead, and zinc (Santore et al., 2001; De Schamphelaere and Janssen, 2002; De Schamphelaere et al., 2002; Heijerick et al., 2002; HDR|HydroQual, 2011; also, see Paquin et al., 2002 for an overview of the BLM). In 2007, the copper BLM became the basis for USEPA's recommended freshwater water quality criteria for copper (USEPA, 2007). The BLM has also been applied to zinc for development of water quality criteria (HydroQual, 2006) but has not yet been approved by USEPA for use for derivation of site-specific water quality criteria. A BLM for lead has recently been developed (HDR|HydroQual, 2011) and will soon be publicly available.

The BLM was used in this study to provide another site-specific line-of-evidence that validates the bioavailability and potential risks associated with dissolved copper, lead, and zinc of Chollas Creek. The USEPA-approved version of the copper BLM was applied to the Chollas Creek WER dataset to derive site-specific BLM-based water quality criteria for dissolved copper. Similarly, the current draft method for derivation of BLM-based water quality criteria estimates for zinc was applied to the same Chollas Creek data. Since a BLM-based method for derivation of site-specific water quality criteria does not currently exist for lead, a BLM-based WER was calculated and then applied as a multiplier to the hardness-based water quality criteria for lead. This approach is comparable to one of the original proposed uses for the BLM (Di Toro et al., 2001).

Evaluation of Biotic Ligand Model Results

- The results of the BLM corroborate the results of the WER study indicating that the current waste load allocations (WLAs) using the default CTR formulas are overprotective.

- For both DPR2 and SD8(1), BLM-predicted median lethal concentrations (LC_{50}s) for dissolved copper and dissolved zinc were consistent with measured LC_{50}s.

Recommendations

- The WERs measured in these experiments and the revised lead criteria should be incorporated into the TMDL for Chollas Creek through a Basin Plan amendment. These values present scientifically based SSOs that are protective of beneficial uses following the recommendations of the CTR for metals criteria.

- Weston Solutions, Inc. (WESTON®) recommends use of the more conservative final WERs established for SD8(1) for development of SSOs for both forks of the watershed, 4.64 for dissolved copper and 1.4 for dissolved zinc.

- Future evaluation of TMDL compliance within the Chollas Creek watershed should incorporate these WERs and the revised lead criteria to evaluate their compliance with site-specific WQOs as shown in Table ES-2.

Table ES-2. Recommended Numeric Targets for Specified Metals in the Chollas Creek Watershed

TMDL Criteria	Dissolved Copper	Dissolved Lead	Dissolved Zinc
WLA-CMC (acute)	*(4.64) * (0.96) * {e^[(0.9422 * ln hardness)-1.700]}*0.9*	*{e^*(1.442[ln(hardness)]-1.884)}*0.9	(1.4) * *(0.978)* * *{e^[(0.8473 * ln* hardness) + *0.884*]}*0.9
WLA-CCC (chronic)	*(4.64) * (0.96) * {e^[(0.8545 * ln hardness)-1.702]}*0.9*	*{e^*(1.442[ln(hardness)]-3.421)}0.9	(1.4) * *(0.986)* * {e^[*(0.8473* ln* hardnes*s*) + *0.884*]}*0.9

The natural log and exponential functions are represented as "ln" and "e", respectively.

- Periodic confirmation of the WERs is recommended every five years or after a significant change in the watershed's land-use distribution, a significant implementation of BMPs that may alter discharge characteristics and/or alter watershed hydrodynamics, or in the event toxicity patterns warrant follow-up testing.

1.0   INTRODUCTION

This report presents the results of the Chollas Creek water-effect ratio (WER) study. The study was conducted to develop site-specific water quality objectives (WQOs) for Chollas Creek in accordance with the California Toxics Rule (CTR) for dissolved metals (USEPA, 2002a). The CTR is used for the basis of the Chollas Creek Dissolved Copper, Lead, and Zinc Total Maximum Daily Load (TMDL), which incorporates a provision for developing site-specific objectives (SSOs).

1.1   Site Description

Chollas Creek flows through the city of San Diego, California, and empties to the eastern shoreline of San Diego Bay. The Chollas Creek Watershed encompasses approximately 16,270 acres consisting predominately of urbanized land located within the San Diego County (Figure 1-1). The drainage area to the north fork of the watershed (9,276 acres) is larger than the south fork (6,997 acres). The upper drainage area of the Chollas Creek Watershed includes the cities of Lemon Grove and La Mesa.

The Chollas Creek Watershed is highly urbanized. Land use in the Chollas Creek Watershed is predominantly residential (48%) and roads (22%), as shown in Figure 1-2. The remaining watershed land uses consist of commercial and industrial facilities and landfills (7%), open space (7%), freeways and highways (5%), schools (3.5%), cemeteries (1.5%), and other miscellaneous land uses. The Chollas Creek Watershed includes Chollas Lake, a 16-acre waterbody located north of Highway 94 in the northeast portion of the watershed.

As a consequence of these diverse land uses, there are numerous sources of discharges to Chollas Creek. Residential, industrial, and commercial discharges to Chollas Creek are associated with portions of the cities of San Diego, Lemon Grove, and La Mesa located within the watershed. In addition, Caltrans is responsible for discharges from the California State Highway System, which possesses its own Municipal Separate Storm Sewer System (MS4) Permit (Order No. 99-06-DWQ) (Regional Board, 2007). The Port of San Diego (Port), the Navy, and the County of San Diego each hold jurisdiction over approximately 1% of the Chollas Creek Watershed. A small portion of the watershed consists of tidelands immediately adjacent to San Diego Bay. Some of this tideland area is under the jurisdiction of the Port, and the remainder falls under the jurisdiction of the Navy. The apportionment of Chollas Creek Watershed by discharger is presented in Table 1-1.

Table 1-1. Jurisdictional Apportionment of the Chollas Creek Watershed

Discharger	Portion (%) of the Chollas Creek Watershed [1]
Caltrans	5
City of San Diego	72
City of Lemon Grove	12
City of La Mesa	9
County of San Diego	1
Port of San Diego	1
Navy	1

(1) Approximately 3.5% of the Chollas Creek Watershed is under the jurisdiction of other agencies not named in the 2007 version of the Dissolved Metals TMDL. This Table has not distinguished the jurisdictions of the Dischargers named in the Dissolved Metals TMDL and other agencies.

1.2   Rainfall, Soil Permeability, and Chollas Creek Flows

Rainfall, low soil permeability, and heavy urbanization significantly influence the flows in Chollas Creek. The annual rainfall at Lindbergh Field, a rain gauge located outside of the Chollas Creek Watershed, demonstrates an average of only 10.23 inches, based on a century of historical data. In addition to low rainfall, the Chollas Creek Watershed is generally characterized by poorly draining soils and compacted urban lands based on United States Department of Agriculture Natural Resources Conservation Service surveys (Figure 1-3). Geotechnical investigations conducted by the City of San Diego in 2007 in the Chollas Creek Watershed indicated that soils within the upper 10–20 ft of the surface in the mesa areas generally have a very low permeability, with only soils along the creek demonstrating higher permeability. The topography of the watershed is characterized by generally built-out urbanized mesas with steep side slopes that drain to open canyons (Figure 1-4). The heavy urbanization of the mesas and abundant freeway infrastructure have altered flow characteristics through a significant increase in impervious surfaces and reduced storage and retention of these flows, resulting in increased volume and velocity of storm water flows in Chollas Creek.

Because of low rainfall in the area, Chollas Creek is a dry channel with intermittent inputs of urban runoff from groundwater seeps, lawn-watering, and/or other activities under ambient conditions. During rainfall events in the Chollas Creek Watershed, Chollas Creek flows respond in a relatively short time frame (i.e., hours). Peak flows occur rapidly (i.e., short time of maximum flow volume and velocity) during the rainfall event and then return back to little or no flow, usually within two days. Most rain events and associated flows occur between October and March with little to no rain from April to September.
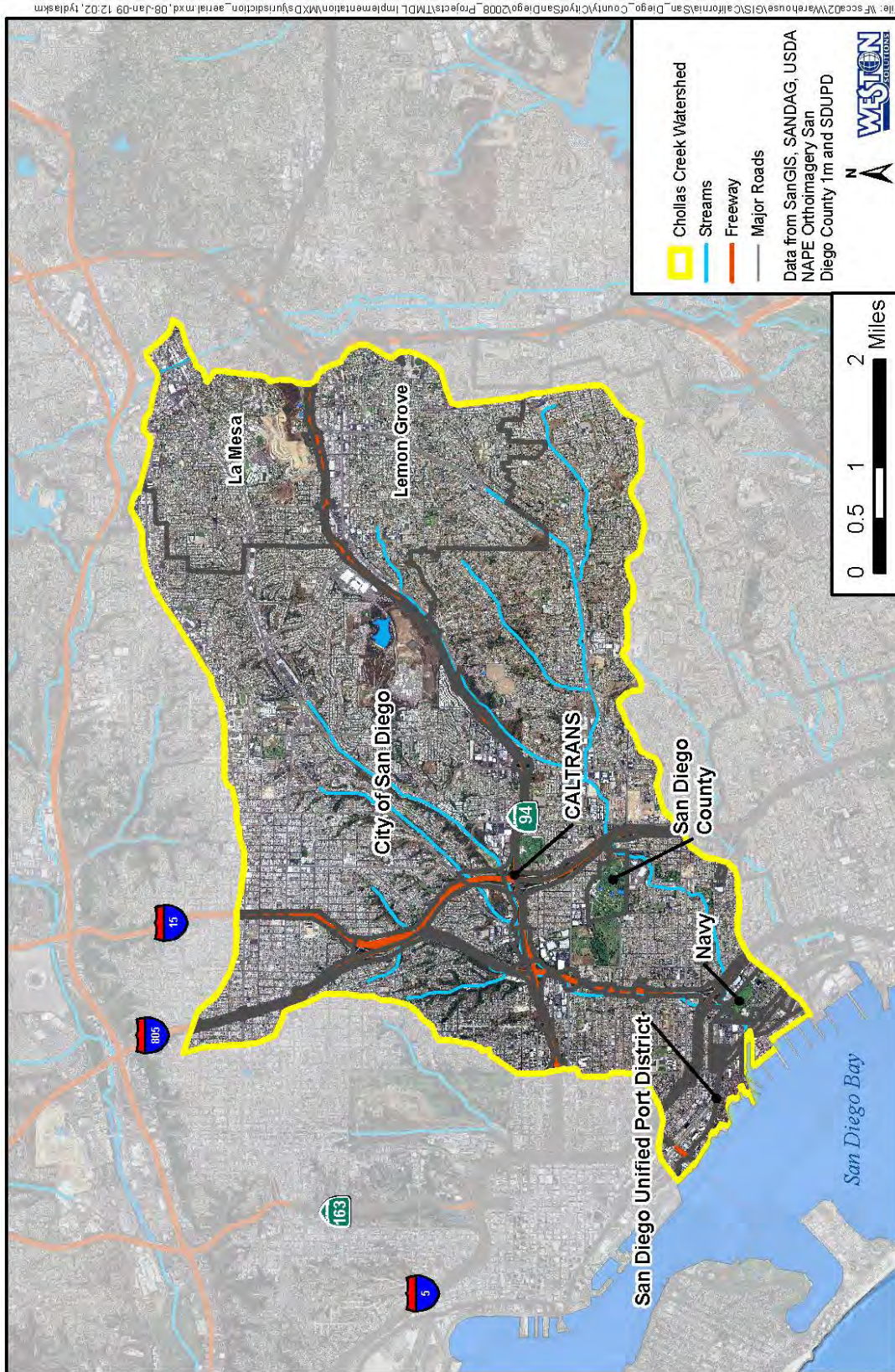
Figure 1-1. Aerial View of the Chollas Creek Watershed
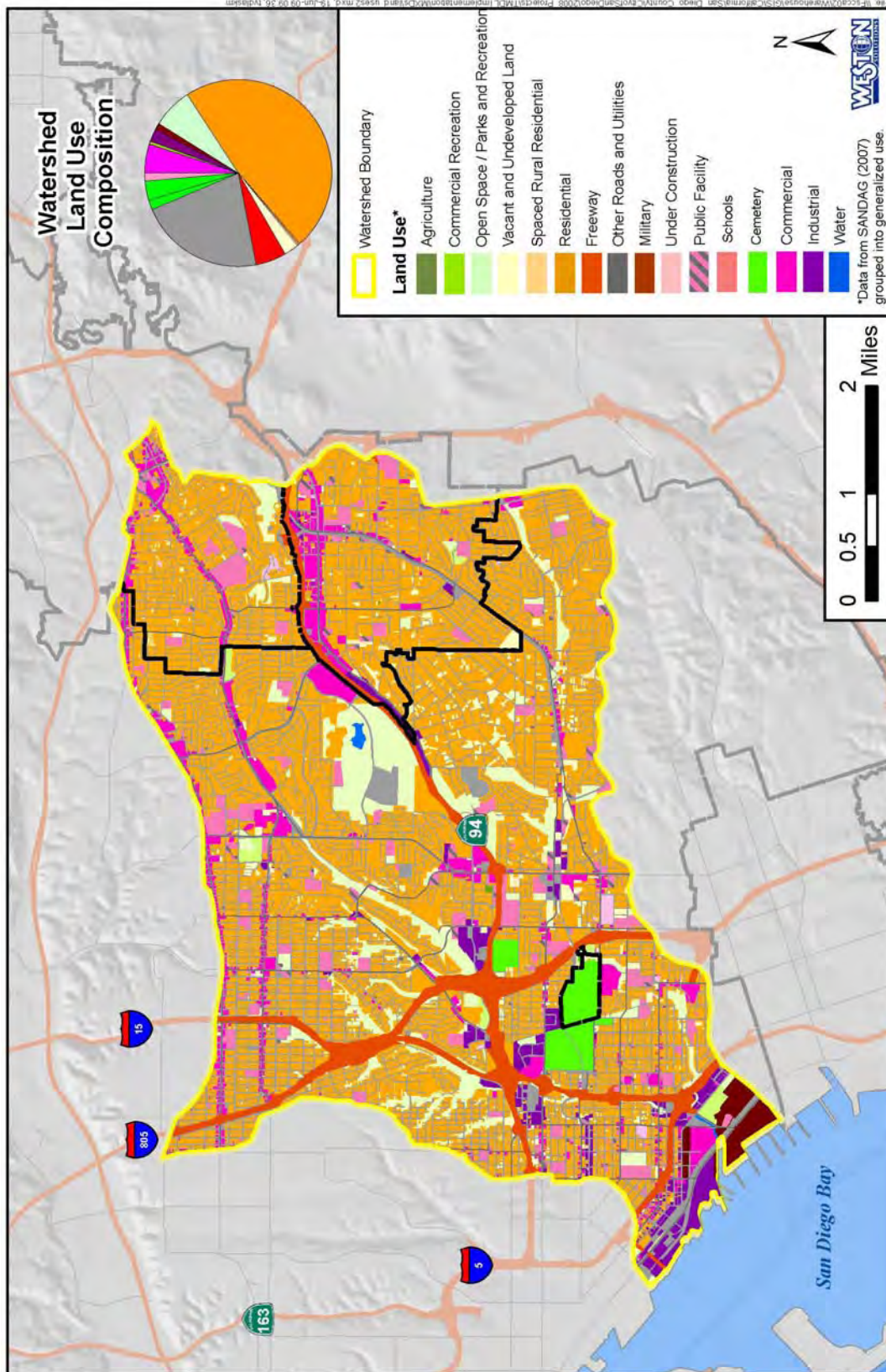
Figure 1-2. Chollas Creek Vicinity and Land Use Map
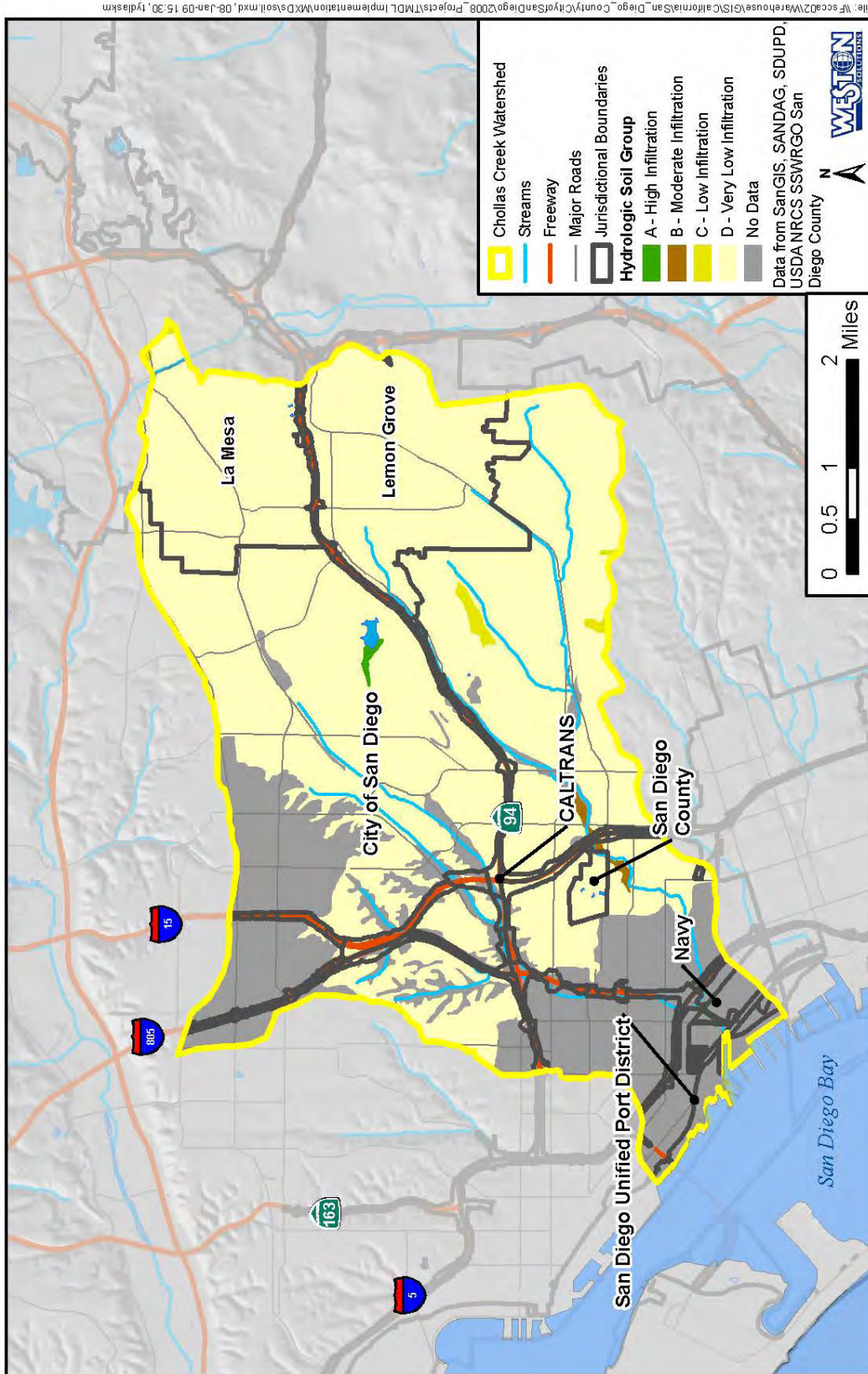
Figure 1-3. Chollas Creek Watershed Soil Permeability
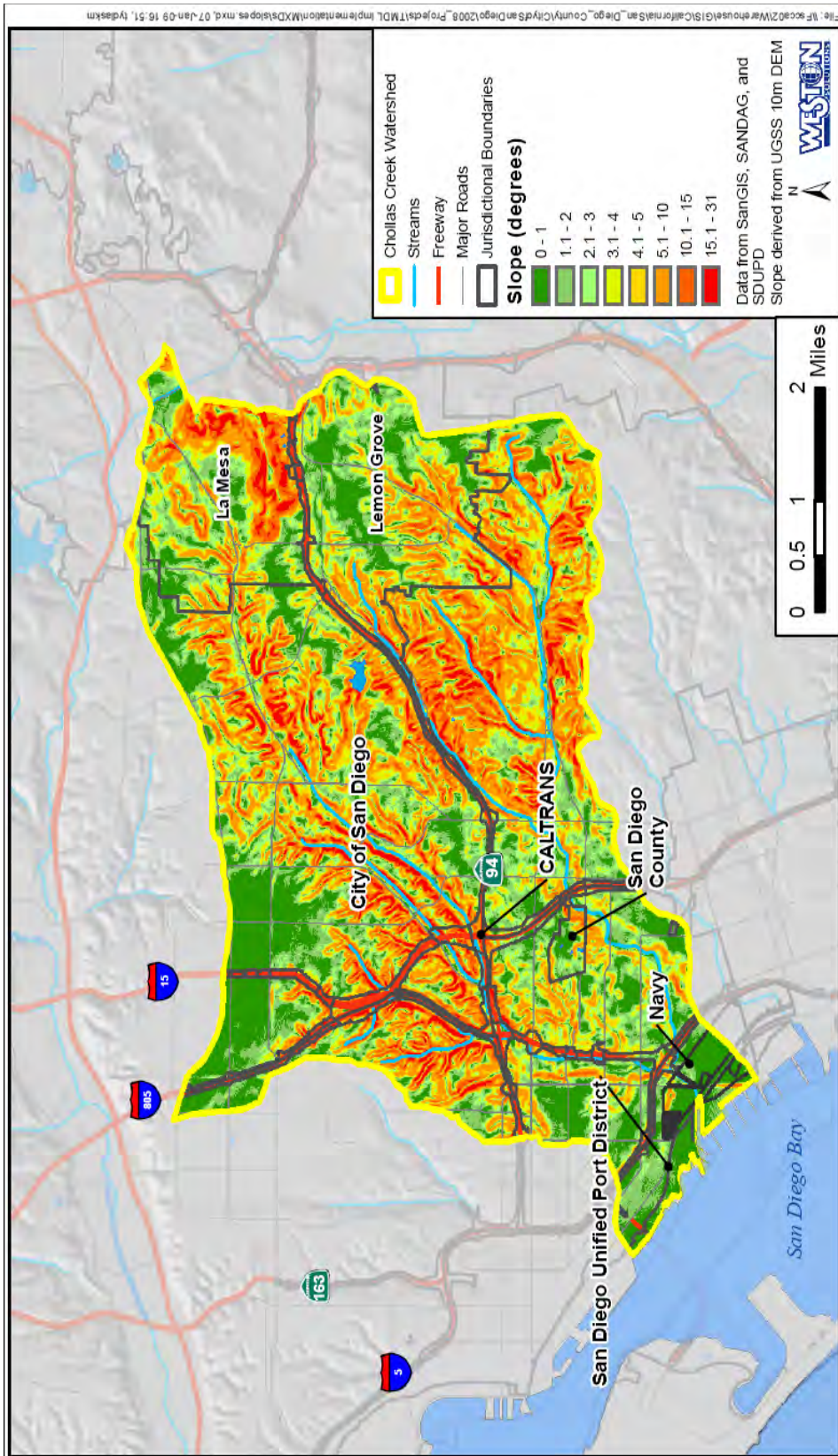
Figure 1-4. Chollas Creek Watershed Slopes

1.3   Chollas Creek 303(d) Listings and Total Maximum Daily Loads

Section 303(d) of the Clean Water Act (CWA) requires that States identify and list water quality-limited segments that do not comply with WQOs and that require TMDLs. TMDLs must then be developed in order to attain applicable WQOs and to restore the beneficial uses of these impaired waters. Consequently, in 1996, the California Regional Water Quality Control Board (Regional Board) placed the lowest 1.2 miles of Chollas Creek (Figure 1-5) on the Section 303(d) list for Diazinon, dissolved cadmium, dissolved copper, dissolved lead, and dissolved zinc for results above the CTR and due to observed toxicity in storm water. In 2002, the watershed was also listed for indicator bacteria (State Board, 2002). However, cadmium was removed from the 2006 proposed Section 303(d) list based on a re-evaluation of the data used for the original listing.

In accordance with federal law, the Regional Board has developed, or is in the process of developing, TMDLs for listed constituents. A TMDL for the organophosphate pesticide Diazinon in Chollas Creek was adopted on August 14, 2002 (Resolution No. R9-2002-0123). Implementation of the *Chollas Creek TMDL for Diazinon* (Diazinon TMDL) was initiated with a phase-out and subsequent full ban on non-agricultural use of Diazinon-based pesticides and fertilizers. Results from this phase-out indicate that the ban has been effective and Diazinon concentrations are trending downward below WQOs. TMDLs for dissolved copper, lead, and zinc were also adopted for inclusion in the Basin Plan on October 22, 2008, by the Office of Administrative Law and United States Environmental Protection Agency (USEPA). TMDLs were finalized for indicator bacteria in Chollas Creek and other regional watersheds on April 4, 2011, by the Office of Administrative Law. Currently, a TMDL is being developed for benthic community effects and sediment toxicity at the mouth of Chollas Creek.
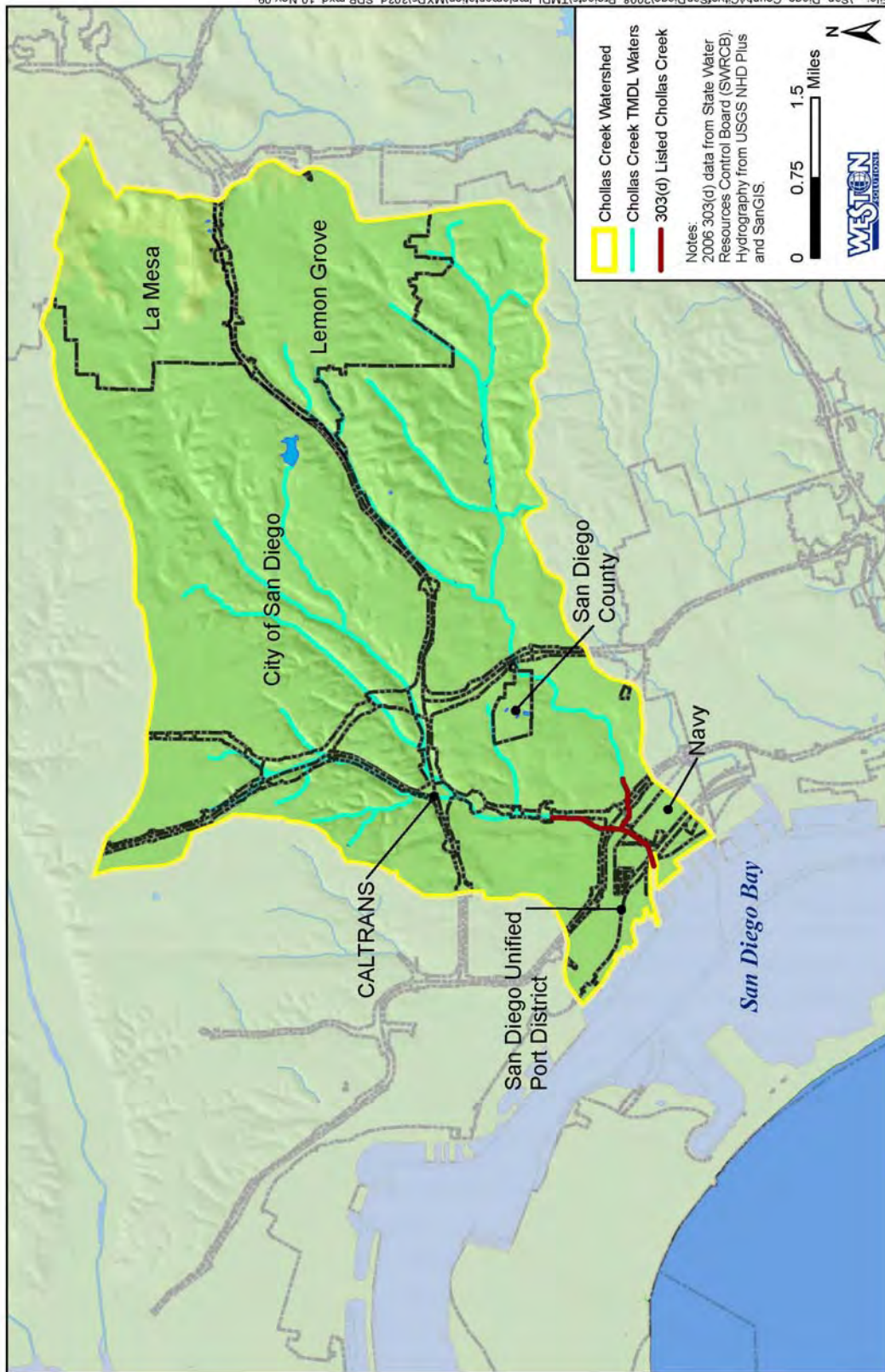
Figure 1-5. Extent of Section 303(d) Listings Overlain with Extent of Total Maximum Daily Loads in the Chollas Creek Watershed

(Data from the 2006 State Water Resources Control Board Section 303(d) Geographical Information Systems Layer)

1.4   Chollas Creek Waste Load Allocations and Numeric Targets in Dissolved Metals Total Maximum Daily Load

The USEPA has established numeric targets for toxic pollutants, which through promulgation of the CTR, were used to develop applicable WQOs for dissolved metals including copper, lead, and zinc. These WQOs are the basis for the Chollas Creek Dissolved Metals TMDL (Table 1-2). The waste load allocations (WLAs) of the Dissolved Metals TMDL are concentration-based and include an explicit 10% margin of safety that takes into account any uncertainties in the TMDL calculation. The WLAs for dissolved copper, lead, and zinc are set equal to 90% of the CTR chronic and acute criteria (Table 1-2). The TMDL also includes an implicit margin of safety due to the conservative assumptions used in developing the criteria for the CTR (Stephan et al., 1985). As a concentration-based TMDL, compliance is not driven by total loads (i.e., flow based), but rather by a measured concentration in the waterbody for which the TMDL applies. Unlike loads, which typically apply in the downstream portions of the watershed, these concentration-based WLAs apply to the entire receiving waters of the Chollas Creek Watershed.

Table 1-2. Water Quality Objectives/ Numeric TMDL Targets for Specified Metals in the Chollas Creek Watershed

Metal	Numeric Target for Acute (CMC) Conditions	Numeric Target for Chronic (CCC) Conditions
Copper (dissolved)	(0.96) * {e^ [0.9422 * ln (hardness) - 1.700]	(0.96) * {e^[0.8545 * ln (hardness) - 1.702]
Lead (dissolved)	{1.46203 – [0.145712 * ln (hardness)]} * {e^ [1.273 * ln (hardness) - 1.460]}	{1.46203 – [0.145712 * ln (hardness)]} * {e^[1.273 * ln (hardness) - 4.705]}
Zinc (dissolved)	(0.978) * {e^ [0.8473 * ln (hardness) + 0.884]}	(0.986) * {e^[0.8473 * ln (hardness) + 0.884]}

Hardness is expressed as milligrams per liter.
The natural log and exponential functions are represented as "ln" and "e," respectively.
CMC=Criteria Maximum Concentration
CCC= Criteria Continuous Concentration

The CTR WQO equations are based on the known inverse relationship between hardness and toxicity. Hardness is a measure of the quantity of divalent ions (i.e., salts with two positive charges) such as calcium and/or magnesium in water. The Chollas Creek TMDL WQOs and numeric targets for dissolved copper, lead, and zinc are based on the CTR criterion for metals. The CTR lists a Criteria Maximum Concentration (CMC) and Criteria Continuous Concentration (CCC) that are calculated using hardness concentrations collected from each sample event to determine the WQOs for each dissolved metal. The CCC and CMC equations for chronic and acute conditions, respectively, are as follows (Regional Board, 2007):

EQUATION 4.1: General Criteria Continuous Concentration

The default value of 1 (most conservative) is used when a site-specific objective has not been determined.

CCC = (WER) * (CFC) * {e^[(mC * ln hardness) + bC]}
Where: CCC = Criteria Continuous Concentration
  WER = Water-Effect Ratio
  CFC = Conversion Factor for freshwater chronic criteria
  mC = slope factor for chronic criteria
  bC = y intercept for chronic criteria

The subscript "c" stands for "chronic" and designates a variable in the CCC equation. The natural log and exponential functions are represented as "ln" and "e," respectively [40 CFR 131.38(b)(2)].

EQUATION 4.2: General Criteria Maximum Concentration

CMC = (WER) * (CFA) * {e^[(mA * ln hardness) + bA]}
Where: CMC = Criteria Maximum Concentration
  WER = Water-Effect Ratio
  CFA = Conversion Factor for freshwater chronic criteria
  mA = slope factor for acute criteria
  bA = y intercept for acute criteria

The subscript "A" stands for "acute" and designates a variable in the CMC equation.
The natural log and exponential functions are represented as "ln" and "e," respectively[40 CFR 131.38(b)(2)].

As shown in the equations above, the WER is a variable of the CCC and CMC equations which can be used to develop an SSO, where:

$$WER = \frac{LC50 \; Site \; Water}{LC50 \; Lab \; Water}$$

Specifically, upon determination of a final WER, SSOs can then be calculated by substituting the final WER value into the CCC and CMC equations for the calculation of site-specific criteria.

2.0   RATIONALE FOR WER STUDY

2.1   USEPA Guidance and Chollas Creek Dissolved Metals TMDL

It is recognized by USEPA that the national criteria for dissolved metals, including those for copper, lead, and zinc, may be more or less protective than anticipated, depending on the site-specific characteristics such as diversity of aquatic life and water quality measurements (i.e., hardness, hydrogen ion concentration [pH], dissolved organic matter, total suspended particulates, and concentrations of contaminants of concern) (USEPA, 1994). As a consequence, USEPA has developed WERs as one of several procedures for deriving an SSO.

As specified in the Chollas Creek Dissolved Metals TMDL, the Regional Board acknowledged that the development of an SSO is an acceptable step in determining appropriate targets for dissolved copper, lead, and zinc in Chollas Creek. The Regional Board also indicated that there are site-specific conditions that could lead to over- or under-protection of the beneficial uses of waterbodies such as Chollas Creek if national criteria are used. The TMDL further indicates that if WER studies and scientific evidence indicate that SSOs are appropriate in Chollas Creek and that the SSOs will protect the beneficial uses of this waterbody, the TMDL will be modified accordingly.

2.2   Historical Metals Exceedances vs. Other Contaminants of Concern and Toxicity in Chollas Creek

Dissolved metals concentrations, monitored for over a decade in Chollas Creek, indicate metal-specific exceedances of CTR values using the default WER value of 1. Since 1994, dissolved copper concentrations in the north fork of Chollas Creek (SD8(1)) have often exceeded the acute and chronic criteria (Figure 2-1). While there also have been dissolved copper exceedances of both acute and chronic criteria in the south fork (DPR2), they occur less frequently and the magnitude of the exceedances is typically less than those in the north fork.

Similar to copper, there have been numerous exceedances of dissolved lead concentrations in the north fork of Chollas Creek. However, lead exceedances have only occurred for the chronic criterion (Figure 2-2). In the south fork only one dissolved lead exceedance (chronic criterion) has occurred since 2004.

There have also been numerous exceedances of dissolved zinc in the north fork of Chollas Creek for both the acute and chronic criteria since 1994 (Figure 2-3). However, dissolved zinc concentrations have not exceeded the acute or chronic criteria in the south fork since 2004.

In addition to metals, the organophosphate pesticide Diazinon was historically elevated in Chollas Creek (Figure 2-4). As discussed in Section 2.1 above, concentrations of Diazinon have decreased to below WQOs as a consequence of the phase-out and full ban on non-agricultural use of Diazinon-based pesticides and fertilizers.

As Diazinon use and its respective Chollas Creek concentrations decreased, pyrethroid use (California Department of Pesticide Regulation, 2004) and subsequent concentrations in Chollas Creek have increased since 2004 (Figure 2-5). It should be noted, however, that due to the lack of proficient analytical techniques and the lack of data prior to 2004 on this class of pesticides, pyrethroid concentrations may have been increasing prior to 2004. Concentrations of representative pyrethroids, bifenthrin and permethrin, are shown to be elevated relative to laboratory derived median lethal concentrations (LC_{50}s) to the freshwater amphipod *Hyalella azteca* (WESTON, 2006; Wheelock et al., 2005).

In addition to analytical measurements of pesticide concentrations, toxicity testing has been conducted on Chollas Creek samples since 2000. As shown in Figure 2-6, Diazinon concentrations are statistically correlated with reproductive toxicity (chronic) to the water flea, *Ceriodaphnia dubia*. The lack of data prior to 2004 precludes a statistical analysis of pyrethroids relative to toxicity to *H. azteca*; however, toxicity identification evaluations (TIEs) provided strong evidence that pyrethroids were the causative agent of toxicity in Chollas Creek after 2005 (Rose et al., 2007). In addition to the presence of pyrethroids measured at concentrations in Chollas Creek storm water samples that exceed the LC_{50} concentrations for *H. azteca*, TIE tests indicated that the causative agent(s) of amphipod toxicity shared all of the physicochemical properties of pyrethroids and lacked properties that characterize other classes of chemicals. For example, the pyrethroid synergist, piperonyl butoxide (PBO) significantly increased toxicity or reduced survival of *H. azteca*, while carboxyl esterase, an enzyme known to metabolize pyrethroids to less toxic forms, significantly reduced toxicity to *H. azteca.*

These results provided evidence that Diazinon, followed by pyrethroids, have likely been the primary causes of toxicity to *C. dubia* and/or *H. azteca*, respectively, over the last decade. Nonetheless, dissolved copper, lead, and zinc were measured in Chollas Creek waters above the default CTR values and required further study to assess the potential for causing toxic effects.
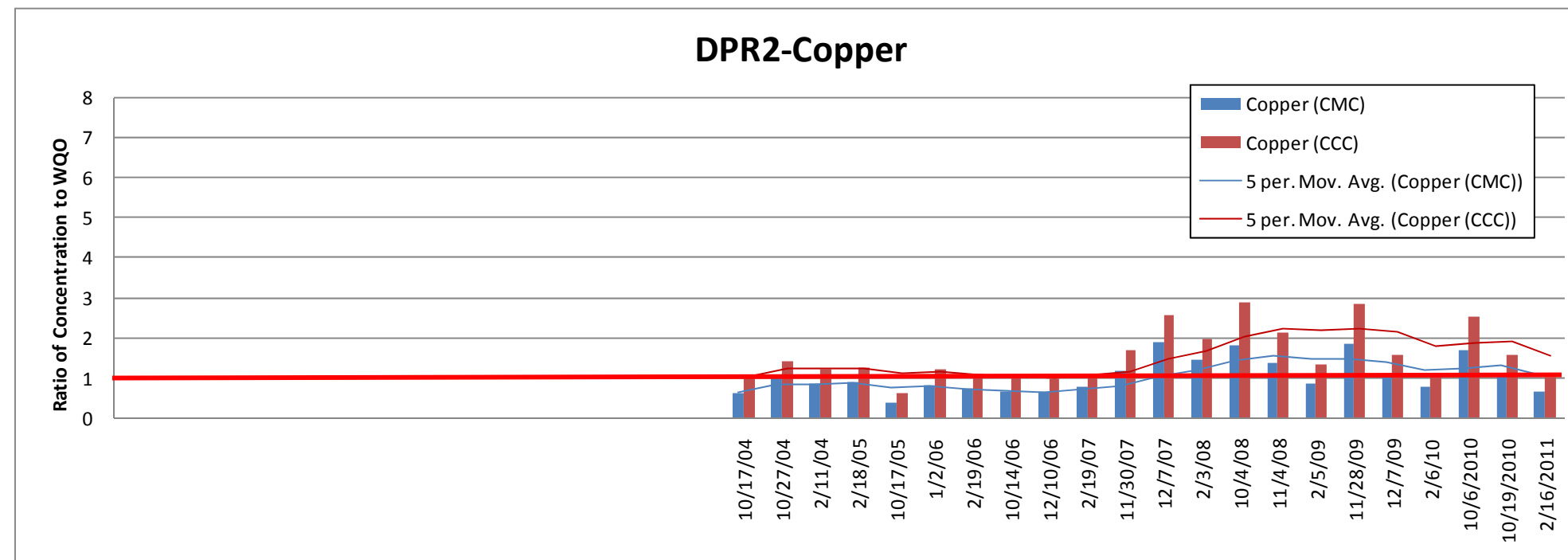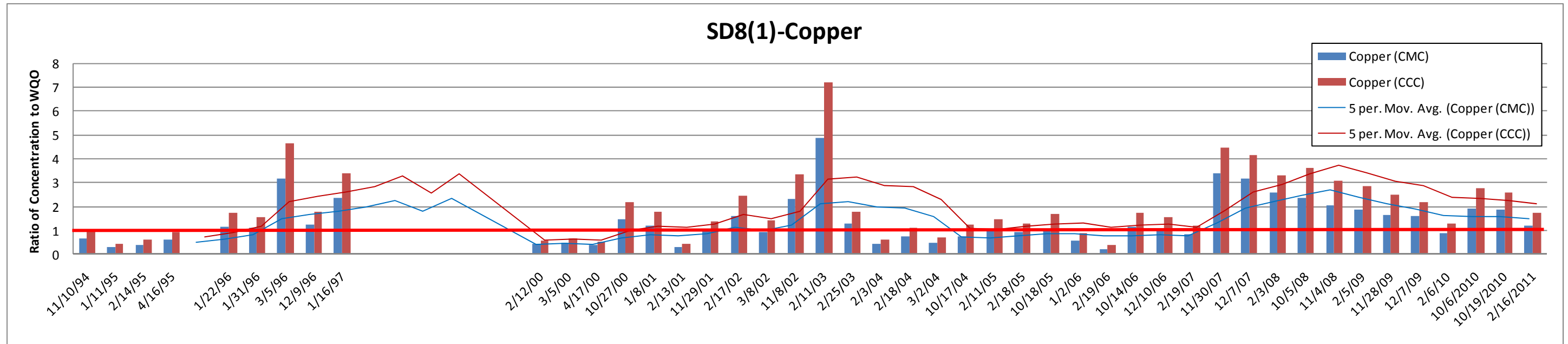
Figure 2-1. Ratio of Dissolved Copper Concentrations Measured in the North Fork (SD8(1)) and the South Fork (DPR2) of Chollas Creek Relative to CCC or CMC

(Values above the red line indicate exceedances of the CMC (blue bars) or CCC (red bars))
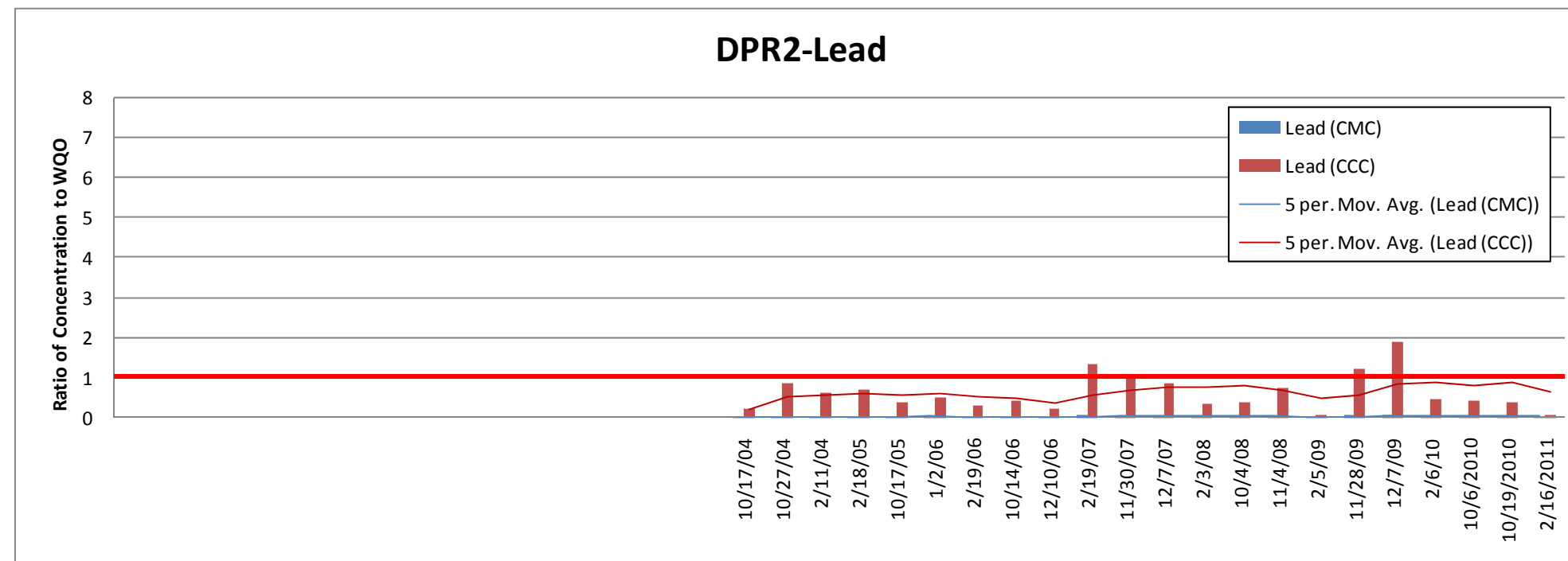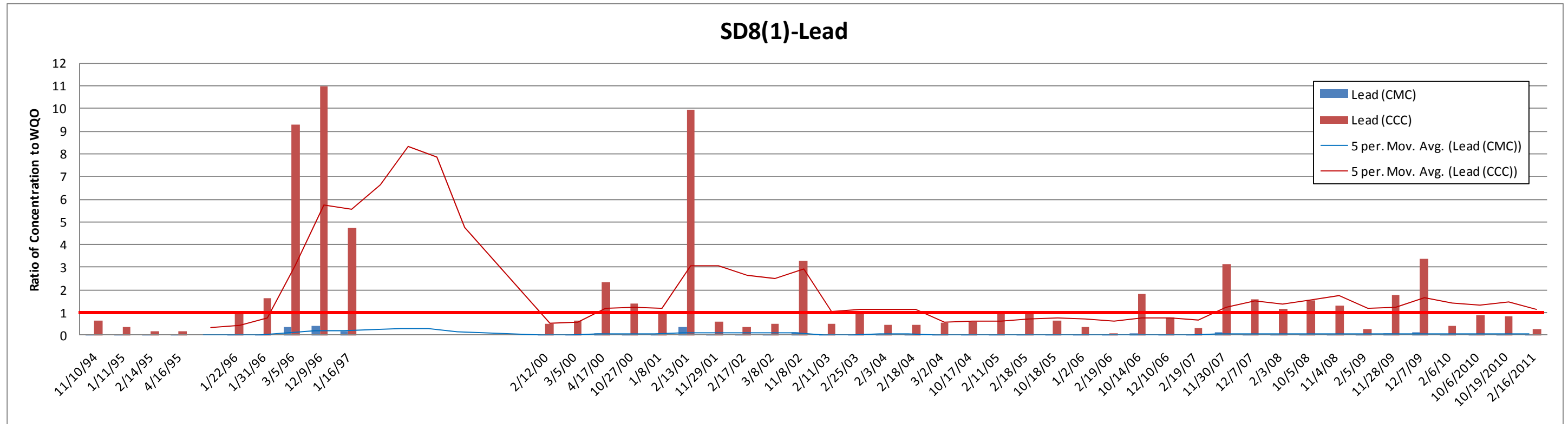
Figure 2-2. Ratio of Dissolved Lead Concentrations Measured in the North Fork (SD8(1)) and the South Fork (DPR2) of Chollas Creek Relative to CCC or CMC

(Values above the red line indicate exceedances of the CMC (blue bars) or CCC (red bars))
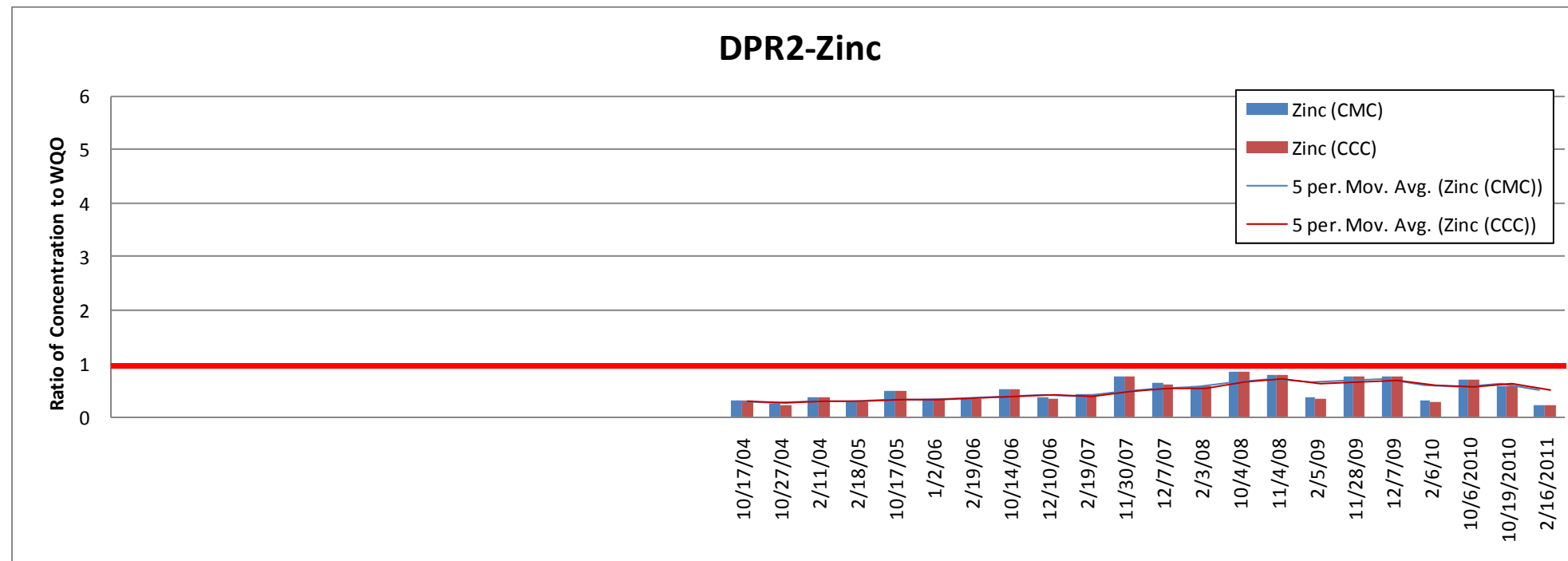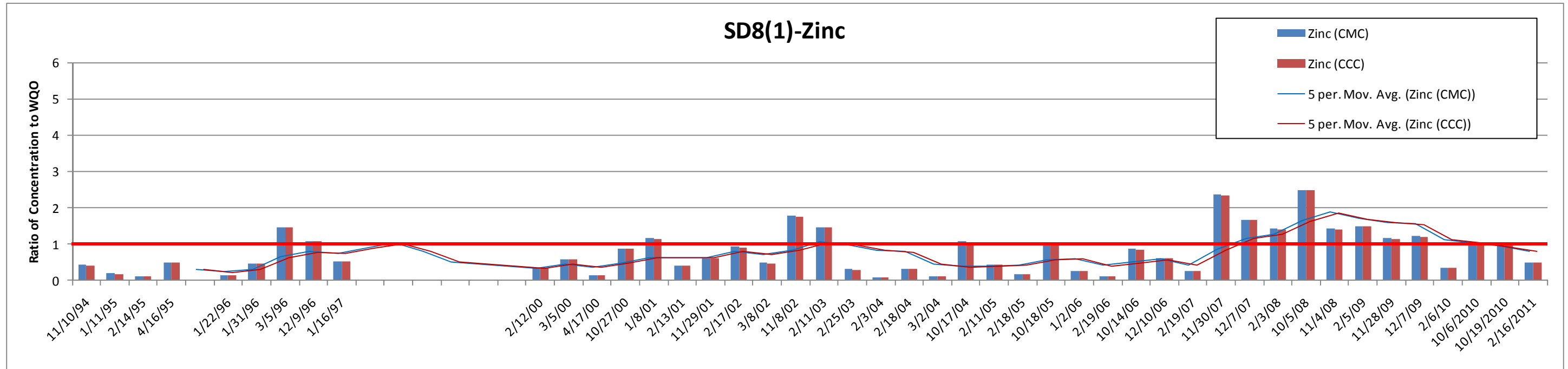
Figure 2-3. Ratio of Dissolved Zinc Concentrations Measured in the North Fork (SD8(1)) and the South Fork (DPR2) of Chollas Creek Relative to CCC or CMC

(Values above the red line indicate exceedances of the CMC (blue bars) or CCC (red bars))
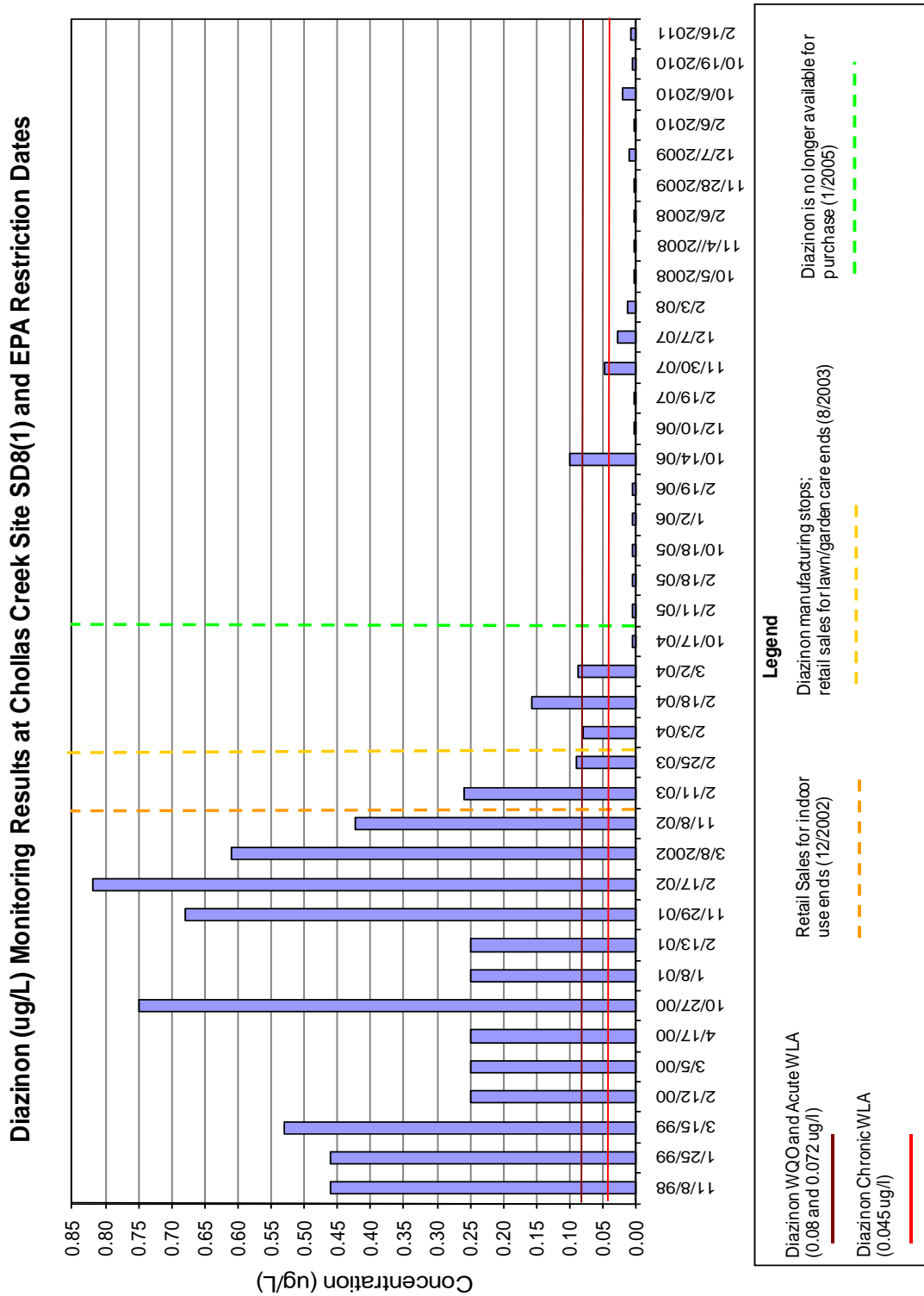
Figure 2-4. Diazinon Concentrations in Chollas Creek Site SD8(1) and USEPA Restriction Dates
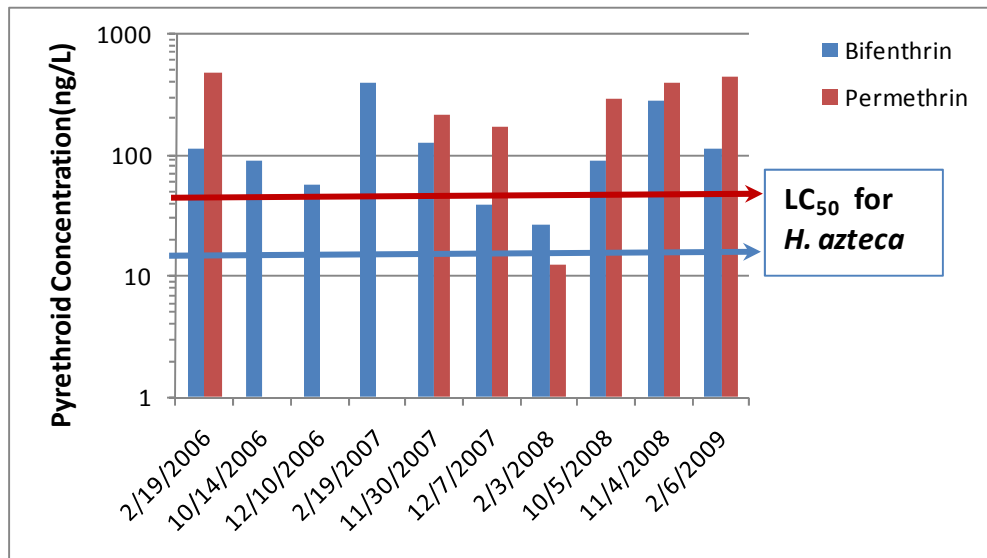
Figure 2-5. Concentrations of Bifenthrin and Permethrin Pyrethroids in Chollas Creek Site SD8(1) and Relevance to the Median Lethal Concentration (LC$_{50}$) of Each Pyrethroid for *Hyalella azteca*
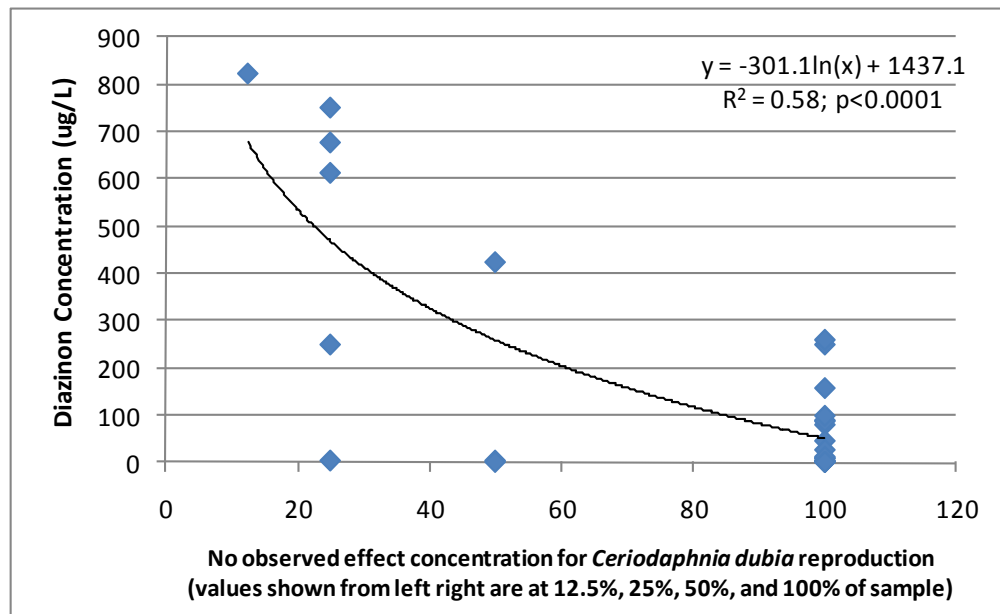
Figure 2-6. Relationship Between Diazinon Concentrations in the North Fork of Chollas Creek and Reproductive Toxicity to *Ceriodaphnia dubia*[1]

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[1] In addition to Diazinon, chlorpyrifos concentrations were also elevated between 2000 and 2005 and may explain some of the variability in this relationship.

2.3   Results of Previous Copper, Lead, and Zinc Water-Effect Ratio Studies

Numerous WER studies have been conducted nationally to determine SSOs for copper, lead, or zinc. The majority of studies were focused on copper (Carlson et al., 1986; S. R. Hansen & Associates, 1992; USEPA, 1992; Diamond et al., 1997a; Diamond et al., 1997b; City of San Jose, 1998; CH2M Hill, 2002; Nautilus Environmental, 2005; Rosen et al., 2005; LWA, 2006; Earley et al., 2007); however, there were several studies which determined WERs for multiple metals including lead and zinc (USEPA, 1992; Diamond et al., 1997b; CH2M Hill, 2002). Results of the reviewed copper WER studies and most of the lead and zinc WER studies demonstrated final WER values that were greater than one. Three of the copper WER studies conducted in California were focused in Southern California. The dissolved copper WER study most relevant to the present study was conducted in Mugu Lagoon and Calleguas Creek (LWA, 2006). Results of this study demonstrated a geometric mean WER of 8.25 for the freshwater invertebrate *C. dubia* in Calleguas Creek and geometric means for the marine mussel *Mytilus galloprovincialis* ranging from 1.51 in Mugu Lagoon (dry weather) to 4.44 in Calleguas Creek (wet weather). These results, together with historical water quality data, suggest that a WER study on Chollas Creek storm water may result in WER values of greater than one.

3.0   OBJECTIVES

The objective of this study was to establish WERs and SSOs for dissolved copper, lead, and zinc, separately, for Chollas Creek. The underlying goal was to determine how much dissolved copper and zinc can be present in Chollas Creek site water without lowering the intended level of protection for Chollas Creek beneficial uses. During the course of development of this program, information regarding a new lead criteria document was made known to the Chollas Creek team by USEPA staff. After review of the draft data tables (C. Delos, USEPA, Personal Communication, April 9, 2010), it was determined that the proposed national criteria for lead re-evaluated the database and used more current scientific methodologies to calculate revised lead criteria. According to the technical advisory committee (TAC) reviewers and other team members, a comprehensive evaluation of the potential effects of these new criteria on the Chollas Creek TMDL for lead was recommended prior to conducting a WER for dissolved lead.

3.1   Water Quality Criteria for Dissolved Lead

A revision to the ambient aquatic life water quality criteria for lead (CAS Registry Number 7439-92-1) has been drafted by the Great Lakes Environmental Center (Traverse City, MI) for the USEPA (2007). In lieu of performing additional sample collection and testing for development of a WER for lead in Chollas Creek as previously proposed, WESTON recommended that a comprehensive review and subsequent analysis of the proposed water quality criteria for lead be performed. This review would include recalculation of the Chollas Creek TMDL using the revised water quality criteria and subsequent comparison of these revised formulas to the Chollas Creek dissolved lead concentrations collected over the previous ten years. In other words, WESTON recommended a comparison of a recalculated TMDL for lead to the current TMDL for lead (2007) and the previous ten years of dissolved lead concentrations

data collected from Chollas Creek and an evaluation of the effect that the new criteria has on the number of acute and chronic exceedances and/or protectiveness shown over time.

This updated document provides guidance to States and Tribes authorized to establish water quality standards under the CWA to protect aquatic life from acute and chronic effects of lead. USEPA is required to publish water quality criteria guidance that accurately reflect the latest scientific knowledge on the identifiable effects on health and welfare that might be expected from the presence of pollutants in any body of water. This draft document of proposed lead criteria was initiated based upon comments received from USEPA staff and independent peer reviewers. The criteria presented in this draft document would supersede previous aquatic life water quality criteria for lead (USEPA 1976, 1980, 1985a) because these new criteria were derived based on the most recent peer-reviewed science.

During the development of the WER study work-plan and based on results from the range-finder tests, it was evident that dissolved lead testing would not be relevant to the low concentrations detected in Chollas Creek. Lead is very insoluble in water and it would require a lower site water and laboratory water pH for lead to be present in solution. However, lowering pH would potentially add confounding factors to the WER tests and would not be relevant to the study. Because the new criteria pose a potential moving target, review of the USEPA draft toxicity calculations was recommended to determine the relevance to the existing criteria. Based on these recommendations and in lieu of performing additional sample collection and testing for development of a Chollas Creek lead WER as previously proposed, a comparison of recalculated CMC and CCC values was conducted using USEPA's revised lead toxicity tables. The dissolved lead CMC and CCC values were recalculated based on current CMC and CCC values for lead and the previous ten years of dissolved lead concentration data collected for compliance monitoring. The effect the new criteria may have on acute and chronic exceedances and/or protection over time was evaluated.

3.2   Biotic Ligand Model

The biotic ligand model (BLM) is a conceptual framework for estimating effects of metals to aquatic organisms (Di Toro et al., 2001; Santore et al., 2001). This framework has been utilized to develop predictive toxicity models for a number of organisms and a number of metals, including copper, lead, and zinc (e.g., Santore et al., 2001; De Schamphelaere and Janssen, 2002; De Schamphelaere et al., 2002; Heijerick et al., 2002; HDR|HydroQual, 2011; also, see Paquin et al., 2002 for an overview of the BLM). The BLM considers the effects of metal speciation, including inorganic and organic complexation, and the effect of competition with cations for binding at idealized biotic ligands on the organism surface.

In 2007, the copper BLM became the basis for USEPA's recommended freshwater water quality criteria for copper (USEPA, 2007). The BLM has also been applied to zinc for development of water quality criteria (HydroQual, 2006), but has not yet been approved by USEPA for use for derivation of site-specific water quality criteria. A BLM for lead has recently been developed (HDR|HydroQual, 2011) and will soon be publicly available.

The BLM was used in order to provide another site-specific line-of-evidence that validates the bioavailability and potential risks associated with dissolved copper, lead, and zinc of Chollas Creek. The USEPA-approved version of the copper BLM was applied to the Chollas Creek WER

dataset to derive site-specific BLM-based water quality criteria for dissolved copper. Similarly, the current draft method for derivation of BLM-based water quality criteria estimates for zinc was applied to the same Chollas Creek data. Since a BLM-based method for derivation of site-specific water quality criteria does not currently exist for lead, a BLM-based WER was calculated and then applied as a multiplier to the hardness-based water quality criteria for lead. This approach is comparable to one of the original proposed uses for the BLM (Di Toro et al., 2001).

3.3   Technical Advisory Committee

A TAC was assembled to provide an outside, independent review of the study design (as described in this report) and study results provided as part of this program. Members of the TAC and their areas of expertise are listed in Table 3-1 below. The TAC performed a review of the draft report and their comments were incorporated and addressed in the final report. Comments on the draft report and the responses are provided in Appendix A.

Table 3-1. Members of the Technical Advisory Committee

TAC Member	Organization	Area of Expertise
Steven Bay	Southern California Coastal Water Research Project	Aquatic Toxicology
Robert Santore	HDR|Hydroqual, Inc.	Metal Bioavailability & Chemistry
Peter Schafer	City of San Jose	Biologist, Water-Effect Ratio

4.0   MATERIALS AND METHODS

4.1   Overview of Chollas Creek Water-Effect Ratio Study

The Chollas Creek WER study was conducted in accordance with the *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals* (USEPA, 1994). This document provided two methods for conducting WERs. Method 1 was designed for determining WERs in streams that are dominated by point-source effluents, downstream of a publically owned treatment works (POTW) or other discharges. Method 2 was designed for determining WERs in large water bodies outside the area of a point source plume or discharge. While neither method was specifically designed for systems comparable to Chollas Creek, in which there are multiple non-point source discharges dominated entirely by urban runoff and storm water, and in which ambient conditions may be completely dry, Method 2 was the more appropriate method for multiple discharges, thus, the design of this study was based on Method 2 guidance.

One of the selected sampling stations (SD8(1)) is near the mouth of the north fork of Chollas Creek where flows represent storm water and urban runoff from the urbanized upstream areas north of this station that is 303(d) listed. The second station (DPR2) is located near the mouth of the south fork of Chollas Creek where flows represent storm water and urban runoff from

urbanized and more natural upstream areas northeast of this station that is 303(d) listed. The north and south fork sites within Chollas Creek were selected because they likely reflect separate sources of contamination and water quality, water quality is well understood, and there is a large database of historical data. Additionally, these two stations are listed as the compliance storm water monitoring stations for the Chollas Creek TMDL Implementation Plan as indicated in Regional Board Order R9-2004-0277. An additional objective of this program will be to determine whether these two stations demonstrate statistically different WERs and, consequently, whether or not a single WER and SSO can be applied to the watershed area.

USEPA guidance suggests that the sampling design for a WER study take into account variability of samples that may occur due to flow (high vs. low), season, temperature, discharge, tidal influence, total suspended solids (TSS) and other water quality variables. As described in Section 1.2, Chollas Creek is a dry channel under ambient conditions with most flow occurring between October and March, with a rainfall-dependent flow level. As a consequence, sampling for this WER study occurred during storm events of varying flows based on rainfall (both high and low flows were captured as part of flow-weighted composite techniques). Chollas Creek WERs are not scheduled to be conducted on water collected under ambient conditions due to the inability to obtain adequate sample volume for testing. Three sampling events occurred in Winter and Spring 2010 (1/18/2010, 2/27/2010, and 4/1/2010) and two additional sampling events occurred in Fall 2010 (10/30/2010 and 12/20/2010) for a total of five flow events at SD8(1) and four flow events at DPR2. It was anticipated that this design would capture variability in dissolved metal WERs associated with temporal seasonality and flow.

To determine the dissolved copper and zinc WERs for Chollas Creek, bioassay testing was conducted with copper and zinc (separately) dissolved in the receiving water samples and in laboratory dilution water. The recommended species and test that was used in this investigation to examine dissolved-metal toxicity was the 48-hour *C. dubia* survival test. This species has been used for compliance testing in Chollas Creek for the last ten years and its toxicity in this creek has consequently been well documented. Thus, results of this study can be compared to historical *C. dubia* toxicity test results. Because of its sensitivity to dissolved metals, this species has been used in numerous studies to establish acute and chronic WERs (USEPA, 1994; Carlson et al., 1986; Diamond et al., 1997b; CH2M Hill, 2002; LWA, 2006). As described in the USEPA WER guidance manual, the most important factor when considering which test and species to use is the sensitivity of the test; of less importance is the duration, species, life-stage, or adverse effect used. Only one species is proposed for WER testing because the more recent USEPA *Streamlined Water-Effect Ratio Procedure for Discharges of Copper* guidance manual states that the secondary species requirement recommended in the 1994 USEPA guidance has been dropped because the secondary species is usually a less sensitive species (e.g., *Pimephales promelas*) and produces lower, inappropriate WERs (USEPA, 2001). WERs with sensitive test species are more appropriate because they best reflect the bioavailability of the metal at the criterion concentration. In addition, only one species and test (i.e., *C. dubia* acute survival) was used in two recent copper WER studies conducted in Southern California (LWA, 2006; 2008).

Comprehensive chemical analyses were conducted on site water samples to determine if there are other measured chemicals that exceed toxicity thresholds and/or other potential confounding factors not related to metals. In addition, water from each concentration within each bioassay test was analyzed for dissolved copper or zinc at test initiation and termination to determine actual dissolved-metal concentrations used to calculate LC_{50}s and WERs.

4.2 Field Collection Program

WESTON conducted a total of five wet weather sampling/monitoring events. Three wet weather sampling/monitoring events occurred during Winter and Spring 2010. Two additional wet weather sampling/monitoring events occurred during Fall 2010. Samples were collected during both low-flow and high flow events at the two sites. Criteria for wet weather events included a minimum of 72 hours of antecedent dry weather and a minimum of 0.10 inch of rain forecasted within the runoff area. The low-flow event was defined as a storm event between 0.10 inch and 0.50 inch of precipitation and when the flow rate was greater than 20 cfs but less than 100 cfs. Samples were collected as flow-weighted composites initiated at the onset of the storm event (i.e., first flush) to ensure that adequate metals concentrations were present in the sample. Water quality samples were collected in accordance with the approved Quality Assurance Project Plan (QAPP; Appendix B). Samples were also collected as flow-weighted composites from the rising limb of the hydrograph for eight hours. Development of the WER does not require project samples to be collected during the same storm events as ongoing compliance monitoring. WESTON monitors the National Weather Service website (http://www.wrh.noaa.gov/sgx/) for forecasted storms. The posted forecasts, discussions, and quantitative precipitation forecast (QPF) are used to determine if a storm meets the criteria for a potential wet weather event. If the QPF predicts measurable rain greater than 0.10 inch at the coast the day prior to a rain event or within 48 hours of a weekend event, storm event staffing will be notified to be on call and ready to perform monitoring. WESTON also uses infrared satellite imagery, live streaming Next Generation Radar (NEXRAD), and pressure gradient maps to verify the QPF.

4.2.1 Sample Locations

Sampling locations for the Chollas Creek WER study are presented in Table 4-1. This study consists of two sites, SD8(1) and DPR2. SD8(1) is located on the north fork of Chollas Creek. DPR2 is located on the south fork of Chollas Creek. Specific locations are presented in Figure 4-1. These two points are also the compliance monitoring points for the Chollas Creek Dissolved Copper, Lead, and Zinc TMDL. Additionally, water chemistry data from an upstream station within each fork, Lemon Grove (LG-1) and La Mesa (LM-1), were compiled for comparison to downstream sites using the BLM.

Table 4-1. Sample Locations Within Chollas Creek

Location	Site ID	Latitude (WGS 84)	Longitude (WGS 84)
Chollas Creek North Fork	SD8(1)	32.70493°	-117.12132°
Chollas Creek North Fork	LM-1	32.754604°	-117.049039°
Chollas Creek South Fork	DPR2	32.69227°	-117.11232°
Chollas Creek South Fork	LG-1	32.727216°	-117.069756°
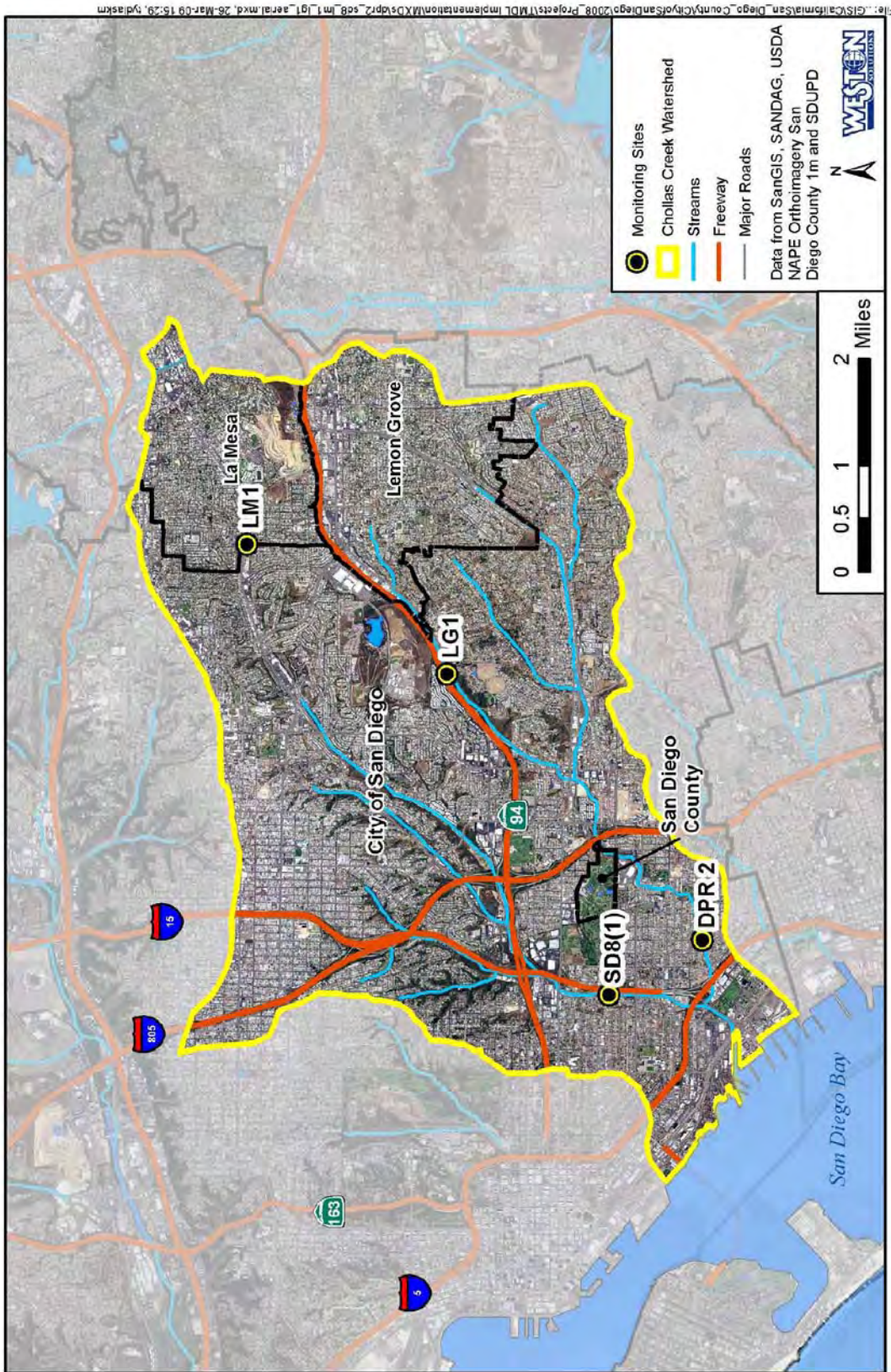
Figure 4-1. Sampling Locations on the North and South Forks of Chollas Creek

4.2.2   Water Quality Sampling and Handling

Water quality samples were collected in accordance with the approved QAPP. Field parameters were collected using an Oakton CON10 pH/conductivity/temperature meter. Samples were collected as grab samples during the Winter-Spring 2010 rainfall event and composited according to the current WER guidelines. Sampling for compliance monitoring at both forks of Chollas Creek was done as flow-weighted samples, consistent with the compliance monitoring methodology. The following sampling protocol outlines the procedures used to collect flow-weighted samples. The final sampling methodology was subject to comment from the Regional Board and was outlined in the final QAPP.

Automated flow and sampling equipment was installed at the site to assist in the collection of flow-weighted composite samples during storm events. An America Sigma flow meter with a pressure transducer or bubbler was installed to measure velocity and stage height. The inflow flow sensor was installed on the channel bottom as near to the center of the channel as possible.

Using the data collected by the flow meter, sample intervals were set to collect approximately 20 L of water over the duration of the sampling period (8 hours). The sample intake point was located adjacent to the flow meter on the channel bottom as near to the center of the channel as possible. An American Sigma automated sampler using a peristaltic pumping mechanism was used to collect 1-L sample aliquots at a sampling rate dependent on measured flow within the Creek. One-liter aliquots were pumped through a Teflon intake device and Teflon tubing into a 20-L borosilicate glass sample bottle for subsequent testing. The sample bottle was set inside an open container that was filled with ice during the storm event. Field crews maintained and replaced the sampling jugs as they filled to capacity.

All water samples were logged on a chain-of-custody (COC) form (Section 4.2.4; Appendix C) and placed in a cooler on ice until delivered to WESTON's laboratory in Carlsbad, California. Upon receipt at WESTON's laboratory, composite samples were sub-sampled in accordance with Table 4-2 for delivery to the appropriate laboratories for chemistry and toxicity analyses. Toxicity analyses were conducted by WESTON's in-house toxicity laboratory located in Carlsbad, California. Chemistry analyses were conducted by CRG Marine Laboratories, Inc. (CRG) in Torrance, California, Weck Analytical Laboratories in City of Industry, California, and Enviromatrix Analytical, Inc. in San Diego, California. Samples were stored at 4°C in the dark until shipped or delivered to the laboratory. All water samples were shipped within 24 hours of collection in the field.

A field data log (Appendix D) was completed by the field team over the course of the storm. The field data log includes empirical observations regarding the site and the storm event (e.g., meteorological conditions, odor, color, turbidity, floating materials, and trash).

Table 4-2. Sample Volume, Container, and Preservative for Laboratory Analyses

Analysis	Volume (mL)	Container	Preservative	Filtering Required
Total Suspended Solids	1,000	HDPE	Cool to 4°C	No
Total Dissolved Solids				
Total Organic Carbon	250	Amber Glass	Cool to 4°C; H_3PO_4	No
Dissolved Organic Carbon	250	Amber Glass	Cool to 4°C	Yes*
Ammonia	250	Amber Glass	Cool to 4°C; H_2SO_4	No
Chloride	500	HDPE	Cool to 4°C	No
Alkalinity				
Sulfate				
Total Hardness	1,000	HDPE	Cool to 4°C; HNO_3**	No
Total Calcium				
Total Magnesium				
Total Sodium				
Total Potassium				
Total Copper				
Total Lead				
Total Zinc				
Dissolved Calcium			Cool to 4°C	Yes*
Dissolved Magnesium				
Dissolved Sodium				
Dissolved Potassium				
Dissolved Copper				
Dissolved Lead				
Dissolved Zinc				
Organophosphorus Pesticides	6 X 1,000	6 Amber Glass	Cool to 4°C	No
Organochlorine Pesticides				
PCB Congeners				
Synthetic Pyrethroids				
PAHs				
48-Hour *C. dubia* Test	10,000	LDPE Cubitainer	Cool to 4°C	No

*For dissolved analysis, filtering occurred in the laboratory upon receipt.
**Total metals and hardness were acidified in the laboratory at CRG.
HDPE = high density polyethylene
LDPE = low density polyethylene
PAHs = polycyclic aromatic hydrocarbons
PCB = polychlorinated biphenyl

4.2.3   Shipping

Prior to shipping, sample containers were placed in sealable plastic bags and securely packed inside the cooler with ice. COC forms were completed (see Section 4.2.4), and the original signed COC forms were inserted in a sealable plastic bag and placed inside the cooler. The cooler lids were securely taped shut and subsequently shipped or delivered to the analytical laboratories listed in Table 4-3.

Table 4-3. Analytical Laboratories and Shipping Information

Laboratory	Volume	Analyses Performed	Point of Contact	Shipping Information
Weston Solutions, Inc. Carlsbad, CA	10 L for *C. dubia* testing	Bioassay testing	Dr. Brian Mastin and Ms. Amy Margolis (760) 795-6901	Weston Solutions, Inc. 2433 Impala Dr. Carlsbad, CA 92010
CRG Marine Laboratories	9.25 L in accordance with Table 2.	Water chemistry	Mr. Eugene Chae (310) 533-5190	CRG Marine Laboratories 2020 Del Amo Blvd., Suite 200 Torrance, CA 90501

4.2.4 Chain-of-Custody Documentation

This section describes the program requirements for sample handling and COC procedures. Samples were considered to be in custody if they were: (1) in the custodian's possession or view, (2) retained in a secured place (under lock) with restricted access, or (3) placed in a secured container. The principal documents used to identify samples and to document possession were COC records, field log books, and field tracking forms. COC procedures were used for all samples throughout the collection, transport, and analytical process, and for all data and data documentation, whether in hard copy or electronic format.

COC procedures were initiated during sample collection. A COC record was provided with each sample or sample group. Each person who had custody of the samples signed the form and ensured that the samples were not left unattended unless properly secured. Minimum documentation of sample handling and custody included the following:

- Sample identification.
- Sample collection date and time.
- Any special notations on sample characteristics.
- Initials of the person who collected the sample.
- Date the sample was sent to the laboratory.
- Shipping company and waybill information.

The completed COC form was placed in a sealable plastic envelope that travelled inside the ice chest containing the listed samples. The COC form was signed by the person transferring custody of the samples. The condition of the samples was recorded by the receiver. COC records were included in the final analytical report prepared by the laboratory and were considered an integral part of that report.

4.3 Water-Effect Ratio Bioassay Testing

To establish the WER for Chollas Creek, bioassay tests were conducted using *C. dubia* in accordance with *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition* (USEPA, 2002b). *C. dubia* 48-hour survival tests were conducted with copper and zinc (separately) dissolved in water from the north and south forks of Chollas Creek (Sites SD8(1) and DPR2, respectively) and in laboratory dilution

water during the wet weather events. The bioassay tests conducted for this study are summarized in Table 4-4.

Table 4-4. Summary of Bioassay Testing for the Chollas Creek Water-Effect Ratio Study

Test Type	Sample	Test Species
		Ceriodaphnia dubia
Rangefinder Tests (1/18/2010)		
Copper spiking	Dilution water	X
	Chollas Creek water (SD8(1))	X
Zinc spiking	Dilution water	X
	Chollas Creek water (SD8(1))	X
Flow Events (02/27/2010, 04/01/2010, 10/30/2010, and 12/20/2010)		
Copper spiking	Dilution water	X
	Chollas Creek water SD8(1)	X
	Chollas Creek water DPR2	X
Zinc spiking	Dilution water	X
	Chollas Creek water SD8(1)	X
	Chollas Creek water DPR2	X
Reference Toxicant Tests		
Copper spiking	Dilution Water	X

4.3.1   Rangefinder Bioassay Testing

Prior to conducting the WER study, WESTON determined a range of metal concentrations to use in subsequent definitive toxicity tests. To do this, six range-finder toxicity tests were performed. Three *C. dubia* rangefinder toxicity tests were conducted for copper and zinc using laboratory dilution water and Chollas Creek water. Results of the rangefinder tests were used to determine a more precise range of concentrations for the actual WER testing and resulted in a more accurate calculation of the LC_{50} and the associated WERs. Test concentrations were prepared by spiking both laboratory and site water with known concentrations of reagent-grade ionic metal salt solutions. Multiple (at least six, including a control) metal concentrations were utilized for each range-finder test. The chemical forms of metals used in the range-finder and all other bioassay testing were copper sulfate (Ricca Chemical Company, CAS # 7758-99-8) and zinc sulfate (Sigma Aldrich, CAS # 7446-20-0), both relatively soluble forms of these metals that are similar to the metal salts used in USEPA's criteria development.

As part of the range-finder bioassay testing, WESTON also evaluated the appropriate hardness of laboratory control water used in the actual WER testing. The hardness of the matched laboratory water was not greater than the hardness of the site water in accordance with WER guidance unless the hardness of the site water was less than 50 mg/L (as $CaCO_3$).

4.3.2   48-Hour *Ceriodaphnia dubia* Bioassay Testing

Forty-eight hour acute bioassays with *C. dubia* were conducted in accordance with USEPA procedures (2002). Testing was initiated within 36 hours of sample collection. During each flow event, 20 *C. dubia* were exposed for 48 hours to a control and seven concentrations of copper and zinc (separately) dissolved in dilution water and water from the north and south forks of

Chollas Creek (sites SD8[1] and DPR2, respectively). The control and each concentration contained four replicates. Water quality was conducted daily and included dissolved oxygen (DO), temperature, pH, and salinity. In addition, water samples were collected from the control and each test concentration at test initiation and completion for metals analyses as described in Section 4.4. Test conditions are summarized in Table 4-5. After 48 hours, the test was considered acceptable if 90% or greater of the test organisms survived in the controls. At test termination, percent survival was calculated for each test concentration.

A 48-hour reference toxicity test was conducted concurrently with the WER study to evaluate the relative sensitivity of test organisms. The reference toxicant test was performed using copper sulfate at total copper concentrations of 3, 6, 12, 24, and 48 µg/L. At test termination, the LC_{50} was calculated and compared to historical laboratory reference toxicant test data for this species.

Table 4-5. Conditions for the 48-Hour Bioassay with *Ceriodaphnia dubia*

Test Conditions		
48-Hour Acute Bioassay		
	Test Species	*Ceriodaphnia dubia*
	Test Procedures	USEPA (2002)
	Age/Size Class	Less than 24 hours
	Test Type/Duration	Acute static non-renewal /48-hours
	Sample Storage Conditions	4°C, dark, minimal head space
	Holding Time	36-hours
	Control Water Source	Dilute water, modified to reflect receiving water hardness
Recommended Water Quality Parameters	Temperature	20 ± 1°C
	Dissolved Oxygen	≥ 4.0 mg/L
	pH	6.0 – 9.0
	Photoperiod	16 hours light, 8 hours dark
	Test Chamber	100 mL
	Concentrations	7 and a control for each metal based on the results of the rangefinder tests
	Replicates/Sample	4
	No. of Organisms/Replicate	5
	Exposure Volume	50 mL
	Aeration	None, unless DO falls below 4.0 mg/L (head space aeration)
	Feeding	*Selenastrum* and cereal leaf extract *ad libitum* at least two hours prior to test initiation
	Water Renewal	None
	Test Acceptability Criterion	90% or greater survival in controls

4.3.3   Quality Assurance / Quality Control

Practices used by WESTON's bioassay laboratory to ensure reliable, high-quality results for the tests conducted for this project are described in the QAPP (Appendix B). The objectives for accuracy and precision involve all aspects of the testing process, including the following:

  ▪ Water sampling and handling

- Source and condition of test organisms
- Condition of equipment
- Test conditions
- Instrument calibration
- Use of reference toxicants
- Record keeping
- Data evaluation

Each test organism was evaluated in reference toxicant tests during the test period to establish the sensitivity of the test organisms. The reference toxicant LC_{50} fell within two standard deviations of the historical laboratory mean. Water quality measurements were monitored to ensure that they fell within prescribed limits and corrective actions (USEPA-recommended) were taken, if necessary. All limits established for this program meet or exceed those recommended by USEPA.

The methods employed in every phase of the bioassay testing program are detailed in WESTON's Standard Operating Practices (SOPs). These SOPs have been audited and approved by an independent, USEPA-recommended laboratory and placed in the quality assurance (QA) files and the laboratory files. All WESTON staff members receive regular, documented training in all SOPs and test methods.

Finally, all data collected and produced as a result of these analyses were recorded on approved data sheets, which become part of the permanent data record of the program. If any aspect of a test deviated from protocol, the test was evaluated to determine whether it was valid according to the regulatory agencies responsible for approval of the proposed permitting action.

4.4   Physical and Chemical Analyses

Due to known historical detections of synthetic pyrethroids, Diazinon, and other potential confounding factors not related to metals, water samples collected from Stations SD8(1) and DPR2 were analyzed for a full suite of constituents (Table 4-6). In addition to the full suite of constituents analyzed on samples SD8(1) and DPR2, an initial and final sample were collected from each concentration of each bioassay test for dissolved and total copper or zinc analysis. The specific metal was based on the bioassay test conducted (i.e., copper spiking or zinc spiking). The control water used in bioassay testing was analyzed for total dissolved solids (TDS), and cations/anions (i.e., sodium, calcium, magnesium, potassium, and chloride). All analytical methods used to obtain chemical concentrations followed USEPA or Standard Methods (SM) (American Public Health Association [APHA], 1998). A summary of the analytical constituent list, including methods, is presented in Table 4-6. The specific analyte lists for organics are presented separately in Table 4-6 through Table 4-11. A summary of analytical methods and laboratory procedures is presented below.

Analyses of trace metals (copper and zinc) and cations (calcium, magnesium, sodium, and potassium) were conducted using an inductively coupled plasma emissions spectrometer equipped with a mass detector (ICP-MS) after acid solubilization in accordance with USEPA 200.8. For determination of dissolved metal analytes, aqueous samples were filtered through a

0.45-µm membrane prior to acid solubilization and analysis by USEPA 200.8. Trace organics (polycyclic aromatic hydrocarbons [PAHs], synthetic pyrethroids, organophosphorus pesticides, organochlorine pesticides, and polychlorinated biphenyl [PCB] congeners) in water were analyzed using gas chromatography and mass spectrometry (GC-MS) in accordance with USEPA Method 625 following serial liquid-liquid extraction with methylene chloride.

Solids were measured by glass fiber filtration of water samples, where the non-filterable residue was dried to a constant at 103-105°C and quantified as total suspended solids in accordance with SM 2540-D. The filtrate was evaporated to a constant dryness at 180°C and quantified as TDS in accordance with SM 2540-C. Organic carbon was measured by catalytic combustion or wet chemical oxidation as total organic carbon (TOC) in accordance with USEPA 415.1. For the determination of dissolved organic carbon (DOC), aqueous samples were filtered through 0.45-µm prior to analysis by USEPA 415.1. Ammonia was measured by the spectrophotometric phenate method in accordance with SM 4500-NH$_3$ F. Chloride was measured by the automated ferricyanide method in accordance with SM 4500-Cl E. Sulfate was measured using the turbimetric method in accordance with 4500-SO$_4^{2-}$ E. Total hardness was determined by calculation using concentrations of calcium and magnesium determined by ICP-MS. Alkalinity was measured by autoanalyzer in accordance with USEPA 310.2.

Table 4-6. Analytical Constituent List

Analyte	Method	Holding Time	Reporting Limits	Units
Total Suspended Solids	SM 2540-D	7 days	5	mg/L
Total Organic Carbon	USEPA 415.1	28 days	0.2	mg/L
Dissolved Organic Carbon	USEPA 415.1	24 hrs	0.2	mg/L
Total Dissolved Solids	SM 2540-C	7 days	5	mg/L
Ammonia	SM 4500-NH$_3$-F	28 days	0.03	mg/L
Chloride	SM 4500-Cl E	28 days	0.05	mg/L
Total Hardness	SM 2340-B	180 days	5	mg/L
Alkalinity	USEPA 310.2	14 days	5	mg/L
Total Calcium	USEPA 200.8	24 hrs	0.1	mg/L
Dissolved Calcium	USEPA 200.8	24 hrs	0.1	mg/L
Total Magnesium	USEPA 200.8	24 hrs	0.1	mg/L
Dissolved Magnesium	USEPA 200.8	24 hrs	0.1	mg/L
Total Sodium	USEPA 200.8	24 hrs	10	mg/L
Dissolved Sodium	USEPA 200.8	24 hrs	10	mg/L
Total Potassium	USEPA 200.8	24 hrs	10	mg/L
Dissolved Potassium	USEPA 200.8	24 hrs	10	mg/L
Sulfate	SM 4500-SO$_4$-E	24 hrs	0.01	mg/L
Total Copper	USEPA 200.8	180 days	0.8	µg/L
Dissolved Copper	USEPA 200.8	48 hrs	0.8	µg/L
Total Lead	USEPA 200.8	180 days	0.1	µg/L
Dissolved Lead	USEPA 200.8	48 hrs	0.1	µg/L
Total Zinc	USEPA 200.8	180 days	0.5	µg/L
Dissolved Zinc	USEPA 200.8	48 hrs	0.5	µg/L
Organophosphorus Pesticides	USEPA 625	7/40 days	Varies by analyte*	ng/L
Organochlorine Pesticides	USEPA 625	7/40 days	Varies by analyte*	ng/L
PCB congeners	USEPA 625	7/40 days	Varies by analyte*	ng/L

Table 4-6. Analytical Constituent List

Analyte	Method	Holding Time	Reporting Limits	Units
Synthetic Pyrethroids	USEPA 625-NCI	4/40 days	Varies by analyte*	ng/L
PAHs	USEPA 625	7/40 days	Varies by analyte*	ng/L

*See specific analyte lists for organics.

Table 4-7. Analyte List for Organophosphorus Pesticides According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
Azinphos-methyl (Guthion)	10	100	ng/L
Bolstar (Sulprofos)	2	4	ng/L
Chlorpyrifos	1	2	ng/L
Demeton	1	2	ng/L
Diazinon	2	4	ng/L
Dichlorvos	3	6	ng/L
Dimethoate	3	6	ng/L
Disulfoton	1	2	ng/L
Ethoprop (Ethoprofos)	1	2	ng/L
Ethyl Parathion	10	20	ng/L
Fenchlorophos (Ronnel)	2	4	ng/L
Fenitrothion	10	100	ng/L
Fensulfothion	1	2	ng/L
Fenthion	2	4	ng/L
Malathion	3	6	ng/L
Merphos	1	2	ng/L
Methamidophos (Monitor)	50	100	ng/L
Methidathion	10	20	ng/L
Methyl Parathion	1	2	ng/L
Mevinphos (Phosdrin)	8	16	ng/L
Phorate	6	12	ng/L
Phosmet	50	100	ng/L
Tetrachlorvinphos (Stirofos)	2	4	ng/L
Tokuthion	3	6	ng/L
Trichloronate	1	2	ng/L

Table 4-8. Analyte List for Organochlorine Pesticides According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
2,4'-DDD	1	5	ng/L
2,4'-DDE	1	5	ng/L
2,4'-DDT	1	5	ng/L
4,4'-DDD	1	5	ng/L
4,4'-DDE	1	5	ng/L
4,4'-DDT	1	5	ng/L
Aldrin	1	5	ng/L
BHC-alpha	1	5	ng/L
BHC-beta	1	5	ng/L
BHC-delta	1	5	ng/L
BHC-gamma (Lindane)	1	5	ng/L
Chlordane-alpha (Chlordane-cis)	1	5	ng/L
Chlordane-gamma (Chlordane-trans)	1	5	ng/L
DCPA (Dacthal)	5	10	ng/L
Dicofol	50	100	ng/L
Dieldrin	1	5	ng/L
Endosulfan Sulfate	1	5	ng/L
Endosulfan-I	1	5	ng/L
Endosulfan-II	1	5	ng/L
Endrin	1	5	ng/L
Endrin Aldehyde	1	5	ng/L
Endrin Ketone	1	5	ng/L
Heptachlor	1	5	ng/L
Heptachlor Epoxide	1	5	ng/L
Methoxychlor	1	5	ng/L
Mirex	1	5	ng/L
Nonachlor-cis	1	5	ng/L
Nonachlor-trans	1	5	ng/L
Oxychlordane	1	5	ng/L
Perthane	5	10	ng/L
Toxaphene NCI-GCMS	10	50	ng/L

Table 4-9. Analyte List for Polychlorinated Biphenyl Congeners According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
PCB003	1	5	ng/L
PCB008	1	5	ng/L
PCB018	1	5	ng/L
PCB028	1	5	ng/L
PCB031	1	5	ng/L
PCB033	1	5	ng/L
PCB037	1	5	ng/L

Table 4-9. Analyte List for Polychlorinated Biphenyl Congeners According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
PCB044	1	5	ng/L
PCB049	1	5	ng/L
PCB052	1	5	ng/L
PCB056/60	1	5	ng/L
PCB066	1	5	ng/L
PCB070	1	5	ng/L
PCB074	1	5	ng/L
PCB077	1	5	ng/L
PCB081	1	5	ng/L
PCB087	1	5	ng/L
PCB095	1	5	ng/L
PCB097	1	5	ng/L
PCB099	1	5	ng/L
PCB101	1	5	ng/L
PCB105	1	5	ng/L
PCB110	1	5	ng/L
PCB114	1	5	ng/L
PCB118	1	5	ng/L
PCB119	1	5	ng/L
PCB123	1	5	ng/L
PCB126	1	5	ng/L
PCB128	1	5	ng/L
PCB138	1	5	ng/L
PCB141	1	5	ng/L
PCB149	1	5	ng/L
PCB151	1	5	ng/L
PCB153	1	5	ng/L
PCB156	1	5	ng/L
PCB157	1	5	ng/L
PCB158	1	5	ng/L
PCB167	1	5	ng/L
PCB168+132	1	5	ng/L
PCB169	1	5	ng/L
PCB170	1	5	ng/L
PCB174	1	5	ng/L
PCB177	1	5	ng/L
PCB180	1	5	ng/L
PCB183	1	5	ng/L
PCB187	1	5	ng/L
PCB189	1	5	ng/L
PCB194	1	5	ng/L
PCB195	1	5	ng/L
PCB200	1	5	ng/L
PCB201	1	5	ng/L
PCB203	1	5	ng/L

Table 4-9. Analyte List for Polychlorinated Biphenyl Congeners According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
PCB206	1	5	ng/L
PCB209	1	5	ng/L

Table 4-10. Analyte List for Synthetic Pyrethroids According to Method USEPA 625-NCI

Analyte	Method Detection Limits	Reporting Limits	Units
Allethrin	0.5	2	ng/L
Bifenthrin	0.5	2	ng/L
Cyfluthrin	0.5	2	ng/L
Cyhalothrin-lambda	0.5	2	ng/L
Cypermethrin	0.5	2	ng/L
Danitol (Fenpropathrin)	0.5	2	ng/L
Deltamethrin	0.5	2	ng/L
Esfenvalerate	0.5	2	ng/L
Fenvalerate	0.5	2	ng/L
Fluvalinate	0.5	2	ng/L
Permethrin	5	25	ng/L
Prallethrin	0.5	2	ng/L
Resmethrin	5	25	ng/L

Table 4-11. Analyte List for Polycyclic Aromatic Hydrocarbons According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
1-Methylnaphthalene	1	5	ng/L
1-Methylphenanthrene	1	5	ng/L
2,3,5-Trimethylnaphthalene (1,6,7-trimethylnaphthalene)	1	5	ng/L
2,6-Dimethylnaphthalene	1	5	ng/L
2-Methylnaphthalene	1	5	ng/L
Acenaphthene	1	5	ng/L
Acenaphthylene	1	5	ng/L
Anthracene	1	5	ng/L
Benz[a]anthracene (1,2-benzanthracene)	1	5	ng/L
Benzo[a]pyrene	1	5	ng/L
Benzo[b]fluoranthene (3,4-benzofluoranthene)	1	5	ng/L
Benzo[e]pyrene	1	5	ng/L
Benzo[g,h,i]perylene (1,12-benzoperylene)	1	5	ng/L
Benzo[k]fluoranthene (11,12-benzofluoranthene)	1	5	ng/L
Biphenyl	1	5	ng/L
Chrysene	1	5	ng/L
Dibenz[a,h]anthracene (1,2,5,6-dibenzanthracene)	1	5	ng/L
Dibenzothiophene	1	5	ng/L
Fluoranthene	1	5	ng/L

Table 4-11. Analyte List for Polycyclic Aromatic Hydrocarbons According to Method USEPA 625

Analyte	Method Detection Limits	Reporting Limits	Units
Fluorene	1	5	ng/L
Indeno[1,2,3-c,d]pyrene	1	5	ng/L
Naphthalene	1	5	ng/L
Perylene	1	5	ng/L
Phenanthrene	1	5	ng/L
Pyrene	1	5	ng/L

4.4.1 Quality Assurance / Quality Control

Detailed descriptions of quality assurance/quality control (QA/QC) procedures for the chemical analysis of samples for this project are presented in the QAPP (Appendix B) and summarized below.

QA objectives for chemical analysis conducted by the participating analytical laboratories are detailed in their Laboratory QA Manual(s). These objectives for accuracy and precision involve all aspects of the testing process, including the following:

- Methods and SOPs.
- Calibration methods and frequency.
- Data analysis, validation, and reporting.
- Internal QC.
- Preventive maintenance.
- Procedures to ensure data accuracy and completeness.

Results of laboratory QC findings, qualifications and exceptions were reported with the final data. Laboratory accuracy was indicated by analysis of matrix spikes, blank spikes, certified reference material (CRM), and/or recovery surrogates. Matrix spike analyses assess the effect a particular sample matrix had on the accuracy of a measurement. Blank spikes demonstrated performance of the preparation method on a clean matrix, void of potential interferences. CRMs or Standard Reference Materials (SRMs) are pre-homogenized materials of various matrices for which compositional information has been certified by a recognized authority and were used to provide a quantitative assessment of the accuracy of an analytical method or procedure. Where CRMs were unavailable, the recovery of an analyte was estimated by studying the recovery of an added compound or element that was regarded as a pure analyte surrogate for the native analyte, most often used with organic analytical procedures.

Precision was determined by analysis of duplicate matrix spikes, blank spikes, recovery surrogate spikes and/or duplicate test sample analysis. Laboratory contamination introduced during method use was assessed through the analysis of procedural/method blanks. Holding times were also evaluated to determine any effect on the analyte's measured concentration. Any QC samples that failed to meet the specified QC criteria in the methodology or QAPP were identified and the corresponding data were appropriately qualified in the final report.

All QA/QC records for the various testing programs were kept on file for review by regulatory agency personnel.

4.5   Data Review, Management, and Analysis

4.5.1   Data Review

All data were reviewed and verified by participating team laboratories to determine whether all data quality objectives had been met and that appropriate corrective actions had been taken, when necessary. WESTON's QA Officer (Ms. Sheila Holt) was responsible for the final review of all data generated.

4.5.2   Data Management

All laboratories supplied analytical results in both hard copy and electronic formats. Laboratories had the responsibility of ensuring that both forms were accurate. After completion of the data review by participating team laboratories, hard copy results were placed in the project file at WESTON and the results in electronic format were imported into the City's and WESTON's database system.

4.5.3   Data Analysis

For each metal and flow event, initial and final dissolved metal measurements were averaged for each concentration used to calculate an LC_{50} endpoint, in accordance with the WER guidance manual (USEPA, 1994). LC_{50} values or point estimates for each WER test conducted (per flow event, per dissolved metal analyte) were determined using ToxCalc™ v1.1.2 rev H 5.0 (Tidepool Scientific Software, McKinley, CA). Statistical assessments of toxicity were performed at the 95% confidence level ($\alpha = 0.05$) and assumptions regarding equality of variance and distribution were evaluated at the 99% confidence level ($\alpha = 0.01$). Probit or Spearman-Karber analyses were used to calculate LC_{50} values. Both laboratory and site water LC_{50} values used to calculate a WER value were determined using the same type of statistical analysis.

WER values were calculated by dividing each site water LC_{50} by its corresponding laboratory water LC_{50} for each WER event, metal analyte, and species. In accordance with USEPA guidance (USEPA, 1994), WERs from individual sites that were sufficiently similar (i.e., within a factor of 3) may be considered one site and data analyzed accordingly. Student's t-test was used to determine if there were significant differences in mean WER values for each species and metal analyte, determined for the South versus the North Forks of Chollas Creek (Zar, 1999). Water quality parameters measured in site water were also compared to long-term average and median concentrations. The final WER for each dissolved metal was calculated based on the outcome of these statistical tests and in accordance with WER guidance. The final WER was calculated as the geometric mean of some or all of the WERs for each species and metal analyte in accordance with the WER guidance (USEPA, 1994).

4.6   Biotic Ligand Model

Subsequent to establishing reasonable concentration estimates for the necessary BLM input parameters, BLM input files were prepared for copper, lead, and zinc. The BLM was executed by HDR|HydroQual (Syracuse, NY) in toxicity mode (i.e., to predict metal-specific, 48-h LC$_{50}$s for *Ceriodaphnia dubia*) and in water quality criteria mode (i.e., to predict final acute values, CMC, and CCC) to provide dissolved copper and zinc BLM results for each water sample. The BLM accomplishes water quality criteria calculations for copper and zinc by predicting the site-specific final acute value (FAV) for each metal. The CMC is subsequently calculated by dividing the FAV by 2 and the CCC is calculated by dividing the FAV by the acute to chronic ratio (3.22 for copper and 5.327 for zinc).

For lead, a BLM-derived WER was calculated for each site, with the BLM-predicted 48-hour *C. dubia* LC$_{50}$ for the February 2, 2011 dilute mineral water (DMW) sample as the denominator, that is:

$$BLM - derived\ Pb\ WER_i = \frac{BLM - predicted\ 48h\ C.dubia\ LC50_i}{BLM - predicted\ 48h\ C.dubia\ LC50_{DMW\ 02-Feb-2011}},$$

where *i* represents a specific water sample.

This value is analogous to a WER developed from toxicity tests and for this purpose was similarly used as a multiplier to hardness-based water quality criteria.

5.0   MONITORING SUMMARY

Monitoring in Chollas Creek was conducted during five individual storm events for the Chollas Creek WER Study from January 2010 through December 2010.

5.1   2009–2010 Rainfall and Flow Data

Estimation of a representative storm event in San Diego County was based on an evaluation of the long-term data records from the National Weather Service rain gauge located at Lindbergh Field. A typical storm event at Lindbergh Field ranges from 0.19- to 0.57-inch of rain and lasts 6 to 12 hours. Since the depth and duration of a typical storm event varies depending on the monitoring station's location within San Diego County, storm events that were preceded by at least 72 hours of dry weather and were forecast to be greater than 0.10 inch were considered viable events for monitoring.

Event-specific rainfall for the Chollas Creek WER Study at SD8(1) and DPR2 are shown in Table 5-1. The watershed received approximately 11.7 inches of rain during the study period based on the rain gauge at DPR2 (October 1, 2009 – February 28, 2011). The average daily rainfall for the Chollas Creek Watershed is shown on Figure 5-1. Monitored storm events are signified by raindrops on Figure 5-1.

Table 5-1. Rainfall Totals for Monitored Events at SD8(1) and DPR2

Storm Event Date	SD8(1) (inches)	DPR2 (inches)	Event Type
01/18/2010	1.00 *	NS	Rangefinder Test for SD8(1)
02/27/2010	0.60	0.71	WER Event No. 1
04/01/2010	0.54	0.52	WER Event No. 2
10/30/2010	0.25	0.23	WER Event No. 3
12/20/2010	0.7	0.66	WER Event No. 4

* The rain gauge was inoperable in January 2010. Data for DPR2 were used during this period.

NS – not sampled
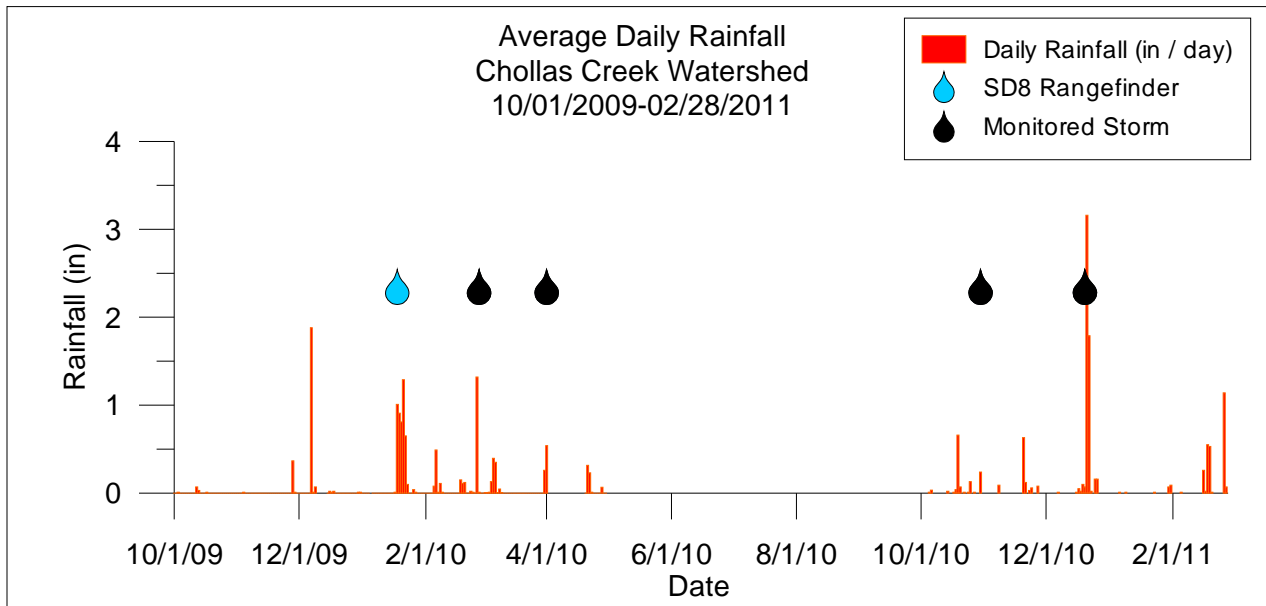
Figure 5-1. 2009–2011 Average Daily Rainfall Totals for the Chollas Creek Watershed

Hydrographs depicting flow rates, rainfall, and sample times for the five storm events monitored at SD8(1) and four storm events monitored at DPR2 are presented in Figure 5-2 and Figure 5-3, respectively.
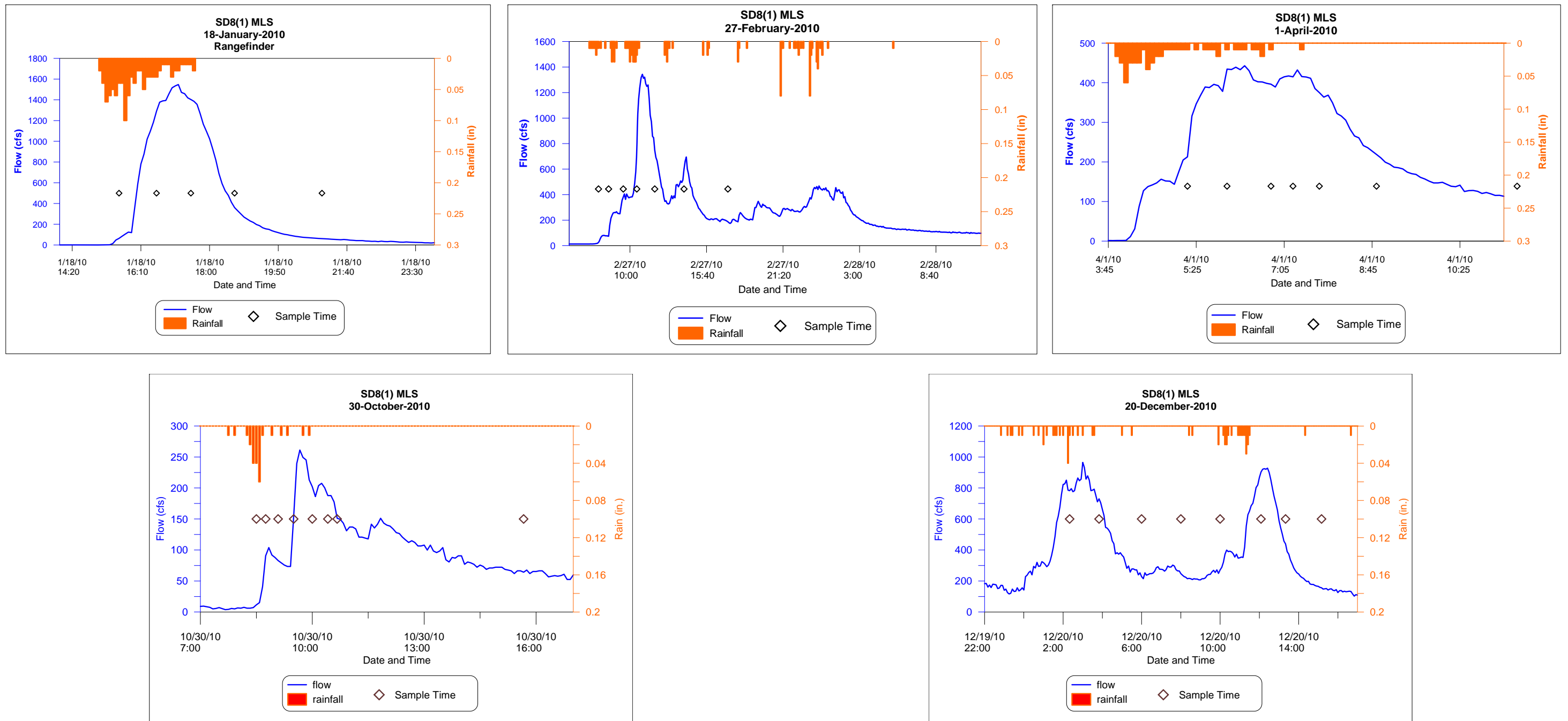
Figure 5-2. 2009–2010 Storm Hydrographs for SD8(1) Mass Loading Station (MLS)
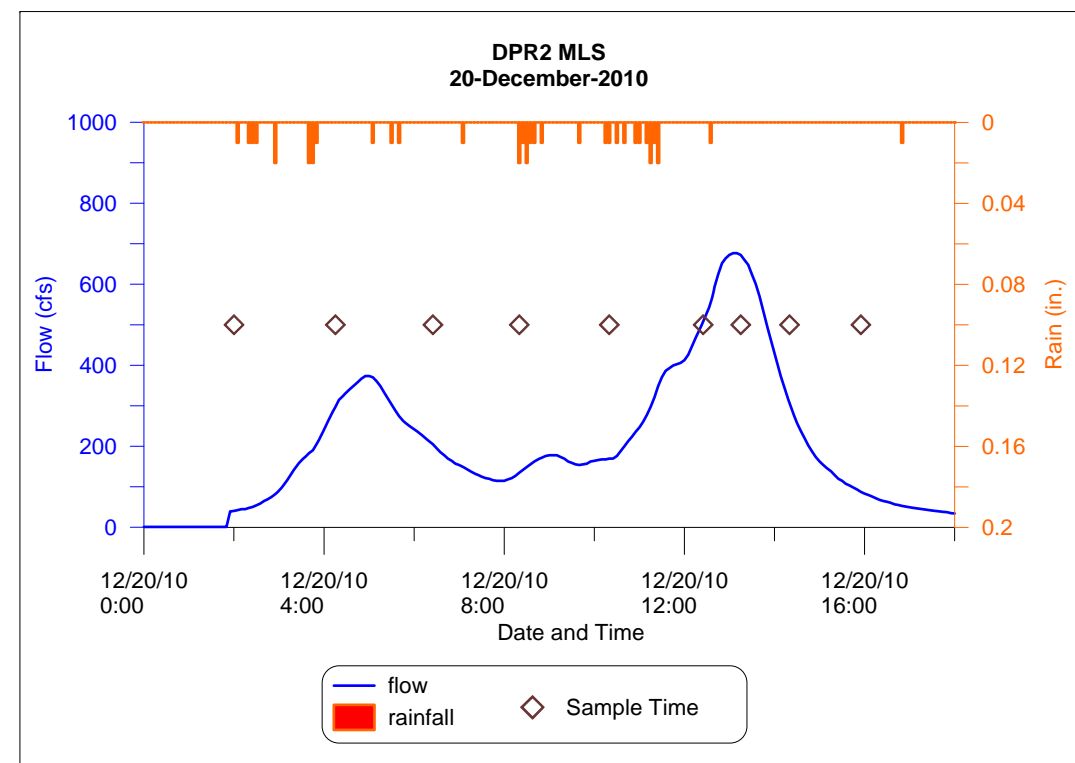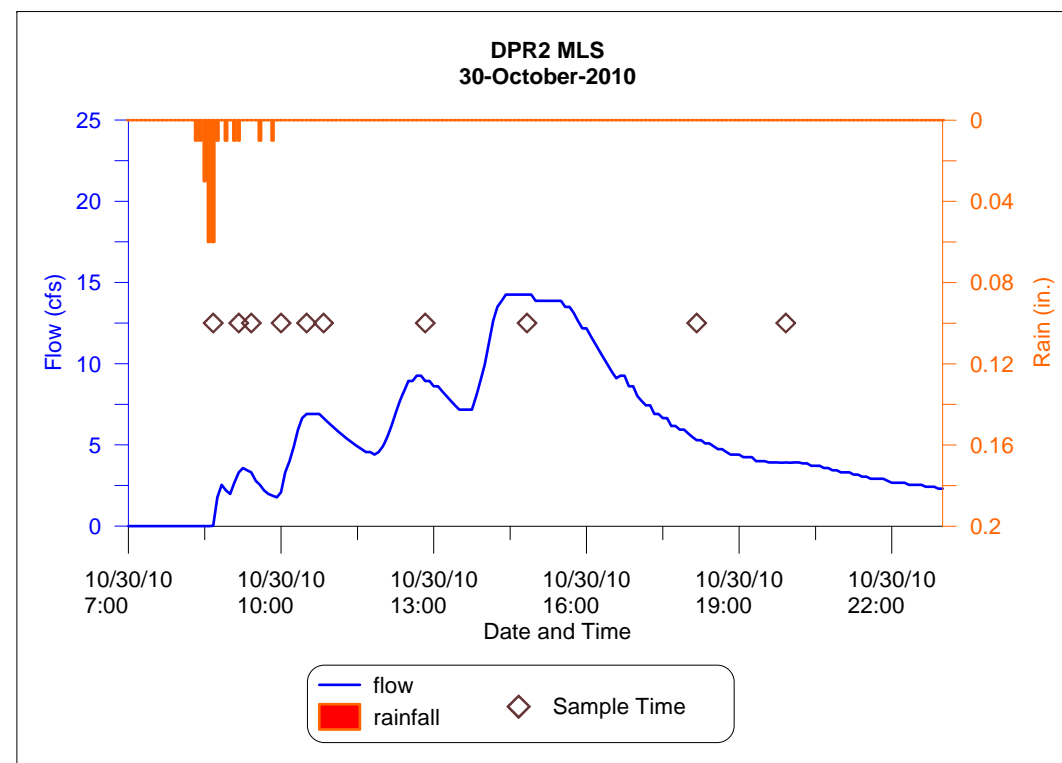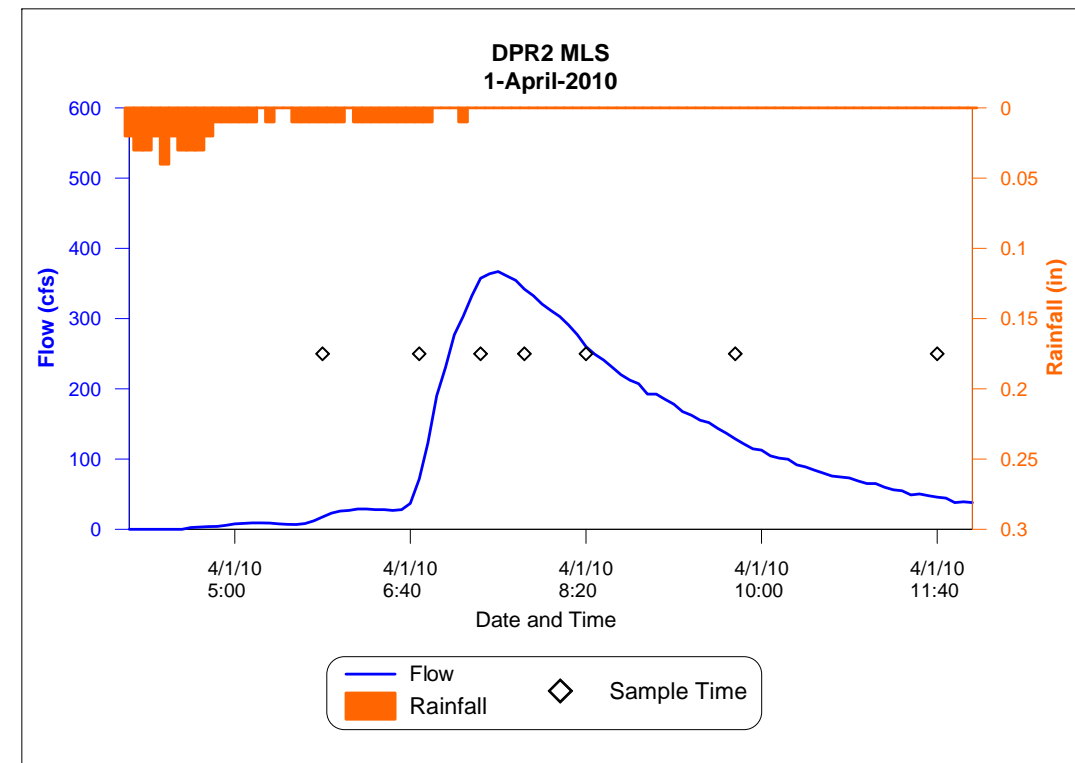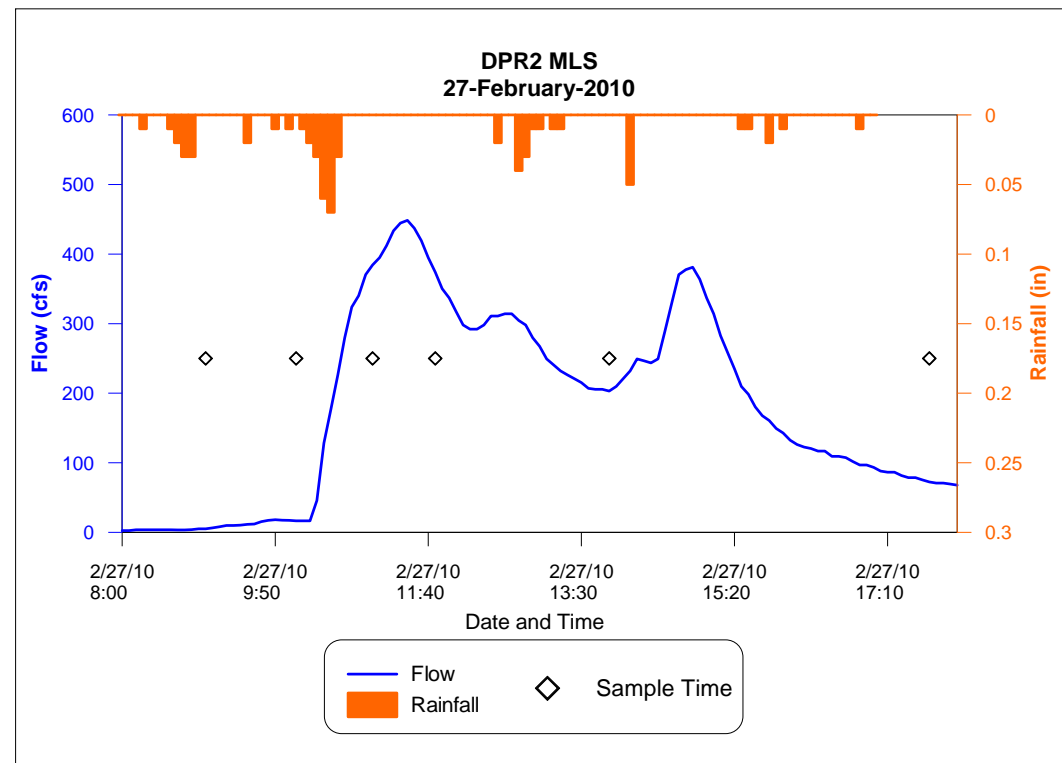
Figure 5-3. 2009–2010 Storm Hydrographs for DPR2 Mass Loading Station (MLS)

6.0   RESULTS

6.1   Analytical Chemistry Results

Analytical chemistry results from the monitored events and laboratory dilutions described in Section 5.0 are presented in Appendix E. Results are presented for the site sample water and for the WER Study dilutions for each metal. The goal of this monitoring was to assess the concentration at which dissolved copper, lead, and zinc influences *C. dubia* toxicity. Additionally, analyses were performed on samples with the goal of running the BLM to compare measured WER results against predicted (modeled) BLM results. The BLM comparisons are presented in Section 8.0. Although no confounding issues were encountered during this study, the additional results provided a backup for investigating any observed toxicity in the raw site water not directly related to metals.

6.1.1   Site Sample Water Results

As mentioned above, raw sample results by event are presented in Appendix E. General chemistry summary statistics are shown in Table 6-1. Results were marginally higher in samples collected from site DPR2 in the South Fork of Chollas Creek than at site SD8(1) in the North Fork, with the exception of sediments (TSS). This is likely due to the slightly higher percent impervious noted in the North Fork of Chollas Creek.

Table 6-1. General Chemistry Summary Statistics from Site Water Collected from Sites SD8(1) and DPR2

Analyte	Units	SD8(1) - Summary Results			DPR2 - Summary Results		
General Chemistry		Min	Max	**Mean**	Min	Max	**Mean**
Ammonia-N	mg/L	0.2	0.5	**0.3**	0.1	0.5	**0.2**
Chloride by IC	mg/L	12.5	27.8	**19.5**	36.0	86.7	**65.1**
Dissolved Organic Carbon	mg/L	3.9	25.2	**11.2**	4.5	28.5	**13.1**
Sulfate by IC	mg/L	10.4	19.8	**14.9**	15.0	35.6	**26.3**
Total Alkalinity	mg/L	26.0	35.0	**31.4**	38.0	66.0	**49.8**
Total Dissolved Solids	mg/L	89.0	140.0	**125.3**	140.0	278.0	**215.0**
Total Hardness as CaCO$_3$	mg/L	22.1	52.0	**39.9**	53.0	103.4	**80.9**
Total Organic Carbon	mg/L	4.7	28.6	**12.2**	5.5	31.3	**14.5**
Total Suspended Solids	mg/L	46.0	322.0	**126.9**	7.0	112.5	**57.6**

Constituents detected in Chollas Creek site waters include general chemistry parameters mentioned above, dissolved metals (e.g., copper and zinc), Chlordane isomers, Malathion, PAHs, and synthetic pyrethroids. PCB congeners were not detected in any samples collected during this study.

Dissolved copper, lead, and zinc and total hardness are the basis for assessing compliance with the Chollas Creek TMDL. Dissolved copper, lead, and zinc and total hardness results for the

WER samples were compared to historical concentrations measured in both forks of Chollas Creek to ensure the samples were representative of historical concentrations. Results are presented as box-whisker plots in Figure 6-1. The boxes show the 25th and 75th percentiles of the data while the whiskers show the minimum and maximum values of the data set. The mean is shown as the line in between the upper and lower percentiles of the data. As shown in Figure 6-1, the concentrations of dissolved copper, lead, and zinc measured during the WER study were within the expected range of the data and were determined to be statistically representative of the historical results. However, the concentrations of total hardness at SD8(1) for the WER Study samples were on the lower end of the range of historical data which would suggest the WER study results and comparisons represent a conservative approach to assessing the SSO.

Chlordane isomers (alpha chlordane, gamma chlordane, cis-nonachlor, and trans-nonachlor) were detected in trace amounts ranging from below detection limit to 32.9 ng/L. Chlordane isomers were not suspected of causing confounding results in this study.

Malathion was detected above the acute benchmark of 430 ng/L in both SD8(1) and DPR during the April 1, 2010 sample event (578 and 480 ng/L respectively). Malathion was also above the chronic benchmark of 100 ng/L during the February 27, 2010 and December 20, 2010 sample event at site DPR2 (153 and 110 ng/L, respectively) and during the October 30, 2010 sample event at both DPR2 and SD8(1) (160 and 110 ng/L, respectively). These detections of Malathion may have played a role in synergistic/additive toxicity observed at both monitored sites, thereby resulting in lower LC_{50}s during these events. The USEPA WER Guidance Document states that a WER is expected to take into account synergistic, antagonistic, and additive toxicity of the site water, and using a WER is more likely to provide the intended level of protection than not using a WER.

Diazinon was only detected in trace amounts at both sites during the December 20, 2010 sample event. Both results were below the Chollas Creek TMDL chronic waste load allocation of 45 ng/L for this constituent. Diazinon was not suspected of causing confounding results in this study.

Detectable quantities of PAHs were observed at both SD8(1) and DPR2. Total PAHs were generally higher at SD8(1) (high of 2,236 ng/L) than DPR2 (high of 557 ng/L). However, results varied widely between sample events. PAHs were similar to those detected in urban runoff where individual analyte values ranged from <1,000 ng/L to upwards of 56,000 ng/L (Caltrans, 2003). More refined values for event mean concentrations were also reported by Caltrans ranging from 300-1,882 ng/L (Caltrans, 2005). PAHs were not suspected of causing confounding results in this study.
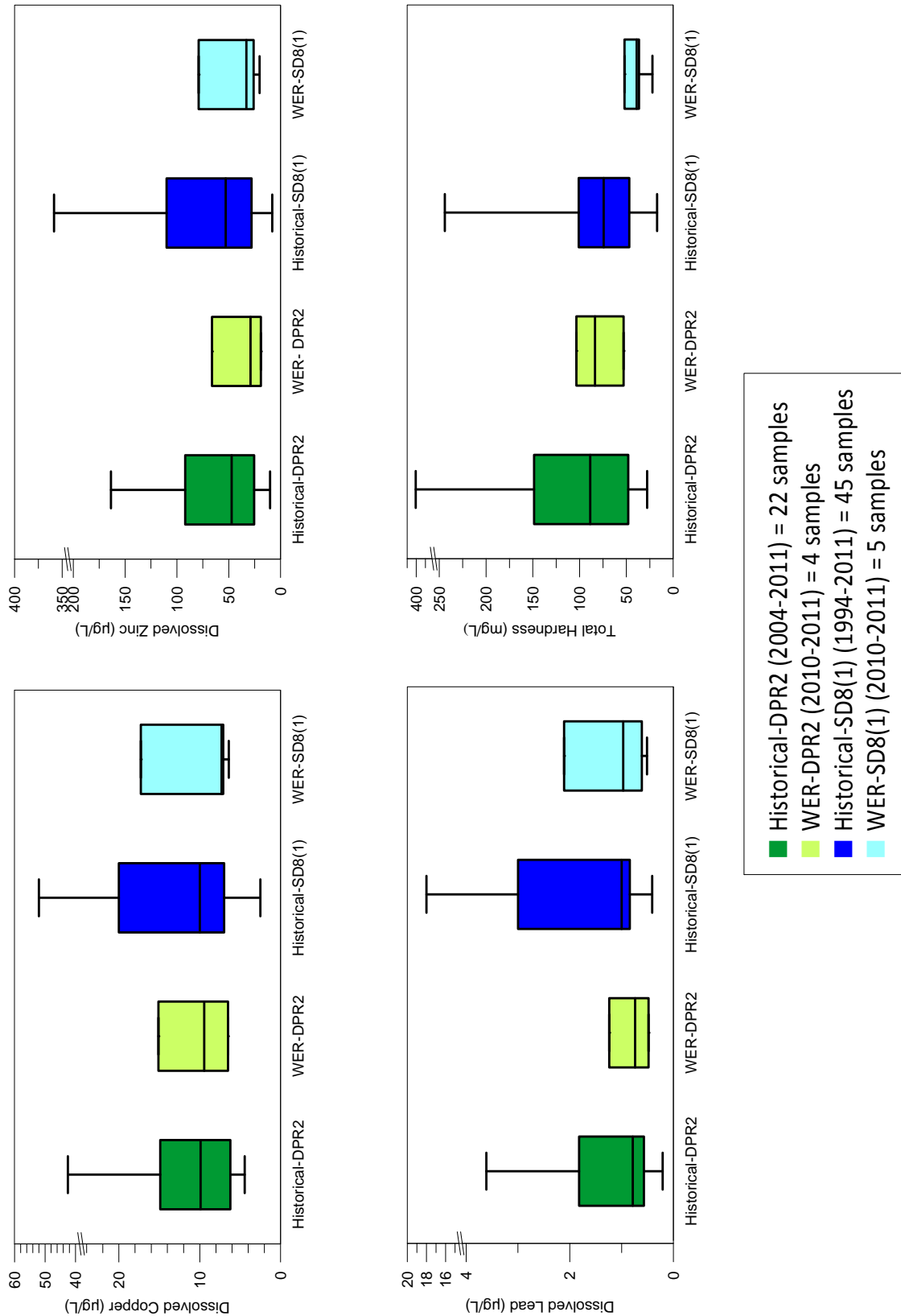
Figure 6-1. Box Whisker Plot of Dissolved Copper, Lead, and Zinc and Total Hardness for Historical Concentrations and WER Study Samples

Synthetic pyrethroids have replaced previously available organophosphate compounds as a result of the ban on Diazinon and Chlorpyrifos by USEPA. Synthetic pyrethroids (i.e., chiefly Bifenthrin, Cyfluthrin, Cypermethrin, and Permethrin) are commonly detected in Chollas Creek runoff. Pyrethroids have also been identified as the causative agent of toxicity to *Hyalella azteca* in previously conducted TIEs in 2006 (WESTON, 2007). Synthetic pyrethroids were detected in potentially lethal concentrations during the January 18, 2010 rangefinder test and the February 27, 2010, April 1, 2010, and December 20, 2010 sample events. Synthetic pyrethroids were also likely detected during the October 30, 2010 sample event, however, due to a laboratory extraction method error, results were not comparable for this event. The City of San Diego also conducted a City Wide Assessment of Synthetic Pyrethroids in 2010, which demonstrated pyrethroids as a common urban runoff pollutant (City of San Diego, 2010). These detections of synthetic pyrethroids may have played a role in enhancing the toxicity observed at both monitored sites, thereby resulting in more conservative WERs being developed during the study.

6.1.2 Water-Effect Ratio Toxicity Test Dilution Series Results

The WER toxicity test results were based on preparing a concentration series for each individual metal for each site water sample. A stock spiking solution was prepared and the initial test and final test metal concentrations (total and dissolved) were measured for each concentration. In order to calculate LC_{50}s, the average of the initial and final dissolved metal concentrations was calculated for use in developing toxicity curves. Sample results from each event are presented in Appendix E. During Event 2, the copper and zinc concentration series were not high enough to induce 50% mortality for site DPR2. Therefore, the dilution series was repeated and additional higher range concentrations were submitted for a re-test.

Variability between initial and final dissolved metal concentrations was evaluated by calculating the relative percent difference (RPD) for each bioassay test concentration. RPD is the relative change in a quantity over a specified time period and the relative percent difference was calculated for each chemical analyte concentration using the following equation:

$$\% \ RPD = \frac{(X1 - X2) \ x \ 100}{(X1+X2)/2}$$

>   where:
>   X1 = measured value of a given analyte from the initial measurement
>   X2 = measured value of a given analyte from the duplicate measurement
>   (X1 + X2)/2 represents the average of the two values

6.1.3   Quality Assurance Summary

Quality assurance/quality control results are included in Appendix E-2. Blank sample results are included in Table 6-2. While detections were noted in the blank samples, results did not suggest that bias was a concern in relation to the spiking samples used for the analysis.

Table 6-2. Blank Sample Analysis Summary

Blank Analysis				
Event	**Site**	**Analyte**	**Fraction**	**Sample Result (µg/L)**
Event No. 1	Blank Water-1	Copper	Total	8
	Blank Water-1	Copper	Dissolved	3
	Blank Water-1	Zinc	Total	59
	Blank Water-1	Zinc	Dissolved	11
Event No. 2	Blank Water-1	Copper	Total	3
	Blank Water-1	Copper	Dissolved	<1
	Blank Water-2	Copper	Total	1
	Blank Water-2	Copper	Dissolved	<1
	Blank Water-1	Zinc	Total	13
	Blank Water-1	Zinc	Dissolved	<0.3
	Blank Water-2	Zinc	Total	32
	Blank Water-2	Zinc	Dissolved	0.48
Event No. 3	Blank Water-1	Copper	Total	1
	Blank Water-1	Copper	Dissolved	<1
	Blank Water-2	Copper	Total	1
	Blank Water-2	Copper	Dissolved	<1
	Blank Water-1	Zinc	Total	12
	Blank Water-1	Zinc	Dissolved	<0.3
	Blank Water-2	Zinc	Total	7
	Blank Water-2	Zinc	Dissolved	1
Event No. 4	Blank Water-1	Copper	Total	2J
	Blank Water-1	Copper	Dissolved	<1
	Blank Water-2	Copper	Total	<0.2
	Blank Water-2	Copper	Dissolved	<1
	Blank Water-1	Zinc	Total	4J
	Blank Water-1	Zinc	Dissolved	1J
	Blank Water-2	Zinc	Total	3J
	Blank Water-2	Zinc	Dissolved	1J

Duplicate results are presented in Table 6-3. For environmental samples, duplicate sample results are considered within an acceptable range of precision if the RPD is less than 20%. RPDs for total metals were all less than 20% with the exception of one sample for copper in Event No. 3 and zinc in Event No. 4. The maximum RPD calculated for dissolved metals was 11.76% suggesting a high level of precision for the sample dilution series analysis.

Table 6-3. Sample Duplicate Analysis Summary

			Duplicate Analysis			
Event	**Site**	**Analyte**	**Fraction**	**Primary Sample (µg/L)**	**Duplicate Sample (µg/L)**	**RPD (%)**
Event #1	DPR2	Copper	Total	105	105	0.00
	DPR2	Copper	Dissolved	75	70	6.90
	DPR2	Copper	Total	75	82	8.92
	DPR2	Copper	Dissolved	64	62	3.17
	SD8(1)	Zinc	Total	1190	1140	4.29
	SD8(1)	Zinc	Dissolved	667	668	0.15
	SD8(1)	Zinc	Total	1270	1210	4.84
	SD8(1)	Zinc	Dissolved	1100	1060	3.70
Event #2	DMW	Copper	Total	24	22	8.70
	DMW	Copper	Dissolved	12	11	8.70
	DMW	Copper	Total	21	22	4.65
	DMW	Copper	Dissolved	10	10	0.00
	DPR2	Copper	Total	132	142	7.30
	DPR2	Copper	Dissolved	110	112	1.80
	DPR2	Copper	Total	114	126	10.00
	DPR2	Copper	Dissolved	96	97	1.04
	SD8(1)	Copper	Total	29.4	29.8	1.35
	SD8(1)	Copper	Dissolved	17.3	17.1	1.16
	DMW	Zinc	Total	192	188	2.11
	DMW	Zinc	Dissolved	137	139	1.45
	DMW	Zinc	Total	196	194	1.03
	DMW	Zinc	Dissolved	141	145	2.80
	SD8(1)	Zinc	Total	323	295	9.06
	SD8(1)	Zinc	Dissolved	138	132	4.44
	SD8(1)	Zinc	Total	247	271	9.27
	SD8(1)	Zinc	Dissolved	130	129	0.77
	SD8(1)	Zinc	Total	161.1	160.3	0.50
	SD8(1)	Zinc	Dissolved	76.6	75.7	1.18
Event #3	DMW	Copper	Total	28	20	33.33
	DMW	Copper	Dissolved	8	9	11.76
	DPR2	Copper	Total	104	104	0.00
	DPR2	Copper	Dissolved	97	99	2.04
	DMW	Zinc	Total	173	174	0.58
	DMW	Zinc	Dissolved	141	140	0.71
	SD8(1)	Zinc	Total	213	205	3.83
	SD8(1)	Zinc	Dissolved	100	98	2.02
Event #4	DMW	Copper	Total	25	27	7.69
	DMW	Copper	Dissolved	11	10	9.52
	DPR2	Copper	Total	121	124	2.45
	DPR2	Copper	Dissolved	75	75	0.00
	DMW	Zinc	Total	180	169	6.30
	DMW	Zinc	Dissolved	149	151	1.33
	SD8(1)	Zinc	Total	195	276	34.39
	SD8(1)	Zinc	Dissolved	73	72	1.38

6.2 Toxicity Results

Toxicity results from each spiking series and event for dissolved copper and dissolved zinc are presented in Tables 6-4 through 6-6. The bioassay lab raw data lab reports are included in Appendix G. The 48-hour *C. dubia* LC_{50} for dissolved copper and zinc at SD8(1) ranged from 59.3 to 195.0 µg/L and 99.9 to 395.6 µg/L, respectively. The 48-hour *C. dubia* LC_{50} for dissolved copper and zinc at DPR2 ranged from 82.4 to 235.0 µg/L and 198.0 to 508.1 µg/L, respectively. The 48-hour *C. dubia* LC_{50} for dissolved copper and zinc in DMW ranged from 3.0 to 13.1 µg/L and 153.7 to 262.3 µg/L, respectively.

6.2.1 Dissolved Copper Water-Effects Ratios

In evaluating the DMW analytical and toxicity results for dissolved copper, it was observed that the LC_{50}s were lower than those values identified by USEPA for *C. dubia*, potentially resulting in an artificially high WER for Chollas Creek. This increased sensitivity to dissolved copper during these experiments may be due to ion imbalance with calcium and magnesium and/or a decreased buffering capacity due to a lack of organic and inorganic ligands. Subsequently, the DMW results for dissolved copper, while still defensible, may result in a less protective SSO. Therefore, WESTON recommends use of the Species Mean Acute Value (SMAV) for *C. dubia* as outlined in the Streamlined Water-Effect Ratio Procedure for Copper (USEPA, 2001). The hardness of DMW samples ranged from 80 to 100 mg $CaCO_3$/L. The more conservative SMAV of 22.11 µg/L for dissolved copper was obtained at a hardness of 100 mg $CaCO_3$/L as listed in the guidance document.

Additionally, measured dissolved copper LC_{50} values for DMW experiments ranged from 3.1 to 5.2 µg/L. These values are considerably lower than BLM-predicted copper toxicity to *C. dubia* (13.4 to 20.8 µg/L) in these same source waters and below BLM-derived CMC and CCC values (discussed further in Section 8.0). Subsequently, the SMAV LC_{50} for *C. dubia* was used in lieu of the LC_{50} determined from the DMW tests as the denominator to calculate the WER for copper. Additional conservatism is recommended in calculation of the final dissolved copper WER for Chollas Creek by using the geometric mean of the recalculated WERs from the most conservative site SD8(1).

The dissolved copper WER (i.e., the site-water median effective concentration (LC_{50}) divided by the laboratory-water LC_{50}) for Site SD8(1) for toxicity experiments conducted on samples from January 18, 2010; February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010 were 6.40, 3.06, 8.82, 4.65, and 2.68, respectively (Table 6-4). The geometric mean (±standard deviation) of the five individual WERs for the north fork of Chollas Creek (i.e., SD8(1)) was 4.64 (2.54), which would be the final WER (Table 6-4).

The dissolved copper WER for Site DPR2 for toxicity experiments conducted on samples from February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010 were 3.73, 10.63, 6.16, and 3.92, respectively (Table 6-4). The geometric mean (±standard deviation) of the four individual WERs for the south fork of Chollas Creek (i.e., DPR2) was 5.56 (3.21), which would be the final WER (Table 6-5).

Table 6-4. Dissolved Copper WERs and 48-Hour *C. dubia* LC$_{50}$s for Laboratory Water (DMW) and Chollas Creek Site SD8(1)

WER event	DMW (µg/L)	SMAV[1] (µg/L)	SD8 (1) (µg/L)	WER w/ DMW-Cu	WER w/ SMAV-Cu
Range Finder (01/18/2010)	13.09	22.11	141.47	10.81	6.40
No. 1 (02/27/2010)	3.05	22.11	67.60	22.14	3.06
No. 2 (04/01/2010)	5.22	22.11	195.01	37.37	8.82
No. 3 (10/30/2010)	4.59	22.11	102.79	22.38	4.65
No. 4 (12/20/2010)	3.77	22.11	59.29	15.75	2.68
Geometric mean (± standard deviation)				**19.94**	**4.64 (2.54)**

[1]USEPA, 2001

Table 6-5. Dissolved Copper WERs and 48-Hour *C. dubia* LC$_{50}$s for Laboratory Water (DMW) and Chollas Creek Site DPR2

WER event	DMW (µg/L)	SMAV[1] (µg/L)	DPR2 (µg/L)	WER w/ DMW-Cu	WER w/ SMAV-Cu
No. 1 (02/27/2010)	3.05	22.11	82.43	27.00	3.73
No. 2 (04/01/2010)	5.22	22.11	235.00	45.03	10.63
No. 3 (10/30/2010)	4.59	22.11	136.21	29.65	6.16
No. 4 (12/20/2010)	3.77	22.11	86.67	23.02	3.92
Geometric mean (± standard deviation)				**30.18**	**5.56 (3.21)**

[1]USEPA, 2001

6.2.2   Dissolved Zinc Water-Effects Ratios

The Site SD8(1) dissolved zinc WER for toxicity experiments conducted on samples from January 18, 2010; February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010 were 2.1, 0.9, 2.6, 1.3, and 0.9, respectively. The geometric mean (±standard deviation) of the five individual WERs for the north fork of Chollas Creek (i.e., SD8(1)) was 1.40 (0.76), which would be the final WER (Table 6-6).

The Site DPR2 dissolved zinc WER for toxicity experiments conducted on samples from February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010 were 1.5, 3.3, 1.2, and 1.1, respectively. The geometric mean (± standard deviation) of the four individual WERs

for the south fork of Chollas Creek (i.e., DPR2) was 1.60 (1.04), which would be the final WER (Table 6-6).

Table 6-6. Dissolved Zinc WERs and 48-Hour *C. dubia* LC$_{50}$s for Laboratory Water (DMW) and Two Chollas Creek Sites (SD8(1) and DPR2)

WER event	DMW (µg/L)	SD8 (1) (µg/L)	SD8 (1) WER-Zn	DPR2 (µg/L)	DPR2 WER-Zn
Range Finder (01/18/2010)	180.00	373.33	2.07	NA	NA
No. 1 (02/27/2010)	178.92	99.89	0.87	262.72	1.47
No. 2 (04/01/2010)	153.71	395.56	2.57	508.11	3.31
No. 3 (10/30/2010)	262.27	349.76	1.33	313.07	1.19
No. 4 (12/20/2010)	176.97	153.79	0.87	198.02	1.12
Geometric mean (± standard deviation)			**1.40 (0.76)**	-	**1.60 (1.04)**

Overall, the final dissolved zinc WERs for SD8(1) and DPR2 were 1.40 and 1.60, respectively. In order to help the City manage a revised dissolved zinc criterion for Chollas Creek, we recommend use of a single, more conservative WER from SD8(1) of 1.40 to be protective of both forks of the creek.

7.0   REVISED LEAD CRITERIA EVALUATION

7.1   Basis for Revised Lead Criteria

7.1.1   State of the Science in Deriving the 1984 Lead Water Quality Criteria

In 1984, USEPA believed that a measurement such as "acid-soluble" lead would provide a more scientifically correct basis upon which to establish criteria for metals (USEPA 1985a). However, at the time, no USEPA-approved methods for such a measurement were available to implement the criteria through the regulatory programs of the Agency. The Agency was considering development and approval of methods for a measurement such as "acid-soluble" lead. Until available, however, USEPA recommended applying the criteria using the total-recoverable method. This had two impacts: (1) certain species of some metals could not be analyzed directly because the total recoverable method did not distinguish between individual oxidation states, and (2) these criteria may be overly protective when based on the total recoverable metal.

Expressing aquatic life criteria for lead in terms of the acid-soluble measurement had both toxicological and practical advantages. On the other hand, because no measurement was known to be ideal for expressing aquatic life criteria for lead or for measuring lead in ambient water or

aqueous effluents, measurement of both acid-soluble lead and total-recoverable lead in ambient water or effluent or both might be useful. For example, there might be cause for concern if total recoverable lead was much above an applicable limit, even though acid-soluble lead was below the limit.

In 1985, Stephan et al. provided an understanding of how the USEPA WQC guidelines were typically applied:

- Acute toxicity test data must be available for species from a minimum of eight diverse taxonomic groups.
- The FAV was derived by extrapolation or interpolation to a hypothetical genus more sensitive than 95% of all tested genera. The FAV, which represents an LC_{50}, was divided by two in order to obtain an acute criterion protective of nearly all individuals in such a genus.
- Chronic toxicity test data (i.e., survival, growth, or reproduction) must be available for at least three taxa. Most often the chronic criterion is set by determining an appropriate acute-chronic ratio and applying that ratio to the acute value of the hypothetical genus more sensitive than 95% of all tested genera. If sufficient data are available to meet the eight diverse taxonomic group minimum, then the chronic value is derived using the same procedure as used for derivation of the FAV.
- When necessary, the acute and/or chronic criterion may be lowered to protect recreationally or commercially important species.
- When evaluating time-variable ambient concentrations generally, one-hour average concentration is considered to be appropriate for comparison with the acute criterion, and four-day averages with the chronic criterion.
- The allowable frequency for exceeding a criterion is set at once every three years, on the average.

USEPA concluded that freshwater aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration (in µg/L) of lead did not exceed the numerical value given by e(1.273[ln(hardness)]-4.705) more than once every three years on the average and if the one-hour average concentration (in µg/L) did not exceed the numerical value given by e(1.273[ln(hardness)-1.460) more than once every three years on the average. For example, at hardnesses of 50, 100, and 200 mg/L (as $CaCO_3$), the four-day average concentrations of lead are 1.3, 3.2, and 7.7 µg/L, respectively, and the one-hour average concentrations are 34, 82, and 200 µg/L.

7.1.2   Summary of 2008 Draft Lead Water Quality Criteria

The water quality criteria for lead in this 2008 draft document will supersede previous criteria for lead because they were derived from science facilitated and published since literature reviews were performed for the 1984 document (USEPA, 2008). Previous aquatic life criteria for lead were expressed in terms of total recoverable lead (USEPA, 1983a) but this measurement was too rigorous in some situations. In 1985, USEPA changed the lead criteria to an operational expression, acid-soluble acid (i.e., the lead that passes through a 0.45-µm membrane filter after the sample is acidified to a pH = 1.5 to 2.0 with nitric acid).

Whenever adequately justified, a national criterion may be replaced by a site-specific criterion (USEPA, 1983b), which may include not only site-specific criterion concentrations (USEPA,

1983c), but also site-specific durations of averaging periods and site-specific frequencies of allowed exceedances (USEPA, 1985b). Such is the case for the acute averaging period for lead. USEPA concluded that all concentrations were to be expressed as lead, not as the chemical tested. The latest literature search for information for this document was conducted in August 2006; some newer information was also used.

Draft 2011 Guidelines for Numerical National Water Quality Criteria for Lead

The current "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (USEPA, 1985a) indicate that freshwater aquatic organisms and their uses should not be affected unacceptably if the four-day average concentration of dissolved lead (in µg/L) does not exceed the numerical value given by $e(1.442[\ln(\text{hardness})]-3.421)$ more than once every three years on the average, and if the 24-hour average concentration (in µg/L) does not exceed the numerical value given by -$e(1.442[\ln(\text{hardness})]-1.884)$ more than once every three years on the average. For example, the four-day average concentrations of dissolved lead criteria calculated at hardness of 50, 100, and 200 mg/L (as CaCO$_3$) are 9.2, 25.0, and 68.0 µg/L, respectively, and the 24-hour average concentrations are 42.8, 116.4, and 316.1 µg/L, respectively.

From the literature, the acute toxicity of lead to several species of freshwater animals has been shown to decrease as the hardness of water increases, so a slope factor was calculated. Adjusted to a hardness of 50 mg/L, the acute sensitivities of 34 species range from 73.80 µg/L total lead for *Diaptomus* (copepod) to 1,569,992 µg/L total lead for *Procambarus* (crayfish). The wide discrepancy between desired nominal exposures and actual measured values was reported for a number of the studies. When measured, dissolved lead comprised the vast majority of the total lead that these test organisms were exposed to during the study.

Data on the chronic effects of lead on freshwater animals were available for four fish and six invertebrate species. The chronic toxicity of lead also decreases as hardness increases as exhibited by the data for *Daphnia magna* provided by Chapman et al. (Manuscript). The lowest and highest available chronic values (11.92 and >405 µg/L total lead) were for an amphipod and smallmouth bass, respectively. Acceptable acute-chronic ratios were available for six freshwater species and range from approximately 5 to 77. Freshwater algae were affected by concentrations of total lead as low as 500 µg/L, based on data for three species.

State Implementation of Water Quality Criterion

A water quality criterion for aquatic life has regulatory impact only when it has been adopted in a state water quality standard for a particular designated use. With the concurrence of the USEPA, states designate one or more uses for each body of water, or segment thereof, and adopt criteria that are consistent with the use(s) (USEPA, 1983a, b, 1987, 1994). State water quality criteria may have the same numerical values as criteria developed under Section 304 of the Clean Water Act or states may adjust water quality criteria to reflect local environmental conditions and human exposure patterns. Alternatively, states may use different data and assumptions than USEPA in deriving numeric criteria that are scientifically defensible and protective of designated uses.

The primary quantitative correlation used to modify lead toxicity estimates is water hardness (USEPA, 1985a). Hardness (i.e., calcium or magnesium ions) almost certainly has some direct effect on lead toxicity (e.g., by influencing membrane integrity). Calcium and magnesium ions compete with divalent metal forms for binding sites on invertebrate and fish gills (Carroll et al., 1979; Evans, 1987; Morel and Hering, 1993; Pagenkopf, 1983). Hardness also serves as a general surrogate for pH, alkalinity, and ionic strength because waters of higher hardness usually have higher pH, alkalinity, and ionic strength. Other parameters such as pH, alkalinity, dissolved organic carbon, humic matter, ionic strength (anions and cations) and dissolved inorganic carbon also affect metal speciation and bioavailability, and thus metal toxicity. Hardness was used here as a surrogate for the ions which affect the results of toxicity tests on lead. It was also recognized that a considerable proportion of dissolved lead in organic-rich waters may be less bioavailable and thus less toxic than freely dissolved lead to aquatic biota. On the other hand, some particulate forms of lead may contribute to lead loading of organisms, possibly through ingestion (Besser et al., 2005; Boenigk et al., 2004).

Site-specific criteria may include not only site-specific criterion concentrations (USEPA, 1994), but also site-specific, and possibly pollutant-specific, durations of averaging periods and frequencies of allowed exceedances (USEPA, 1991). The averaging periods of 24 hours for lead (same as recommended for other metals, e.g., cadmium) and four days were selected by USEPA on the basis of data concerning how rapidly some aquatic species react to increases in the concentrations of some aquatic pollutants. Three years is the Agency's best scientific judgment of the average amount of time aquatic ecosystems should be provided between exceedances (Stephan et al., 1985; USEPA, 1991). Various species and ecosystems react and recover at greatly differing rates, thus with adequate justification, site-specific and/or pollutant-specific concentrations, durations, and frequencies may be higher or lower than those given in national water quality criteria for aquatic life.

Whenever scientifically justified, site-specific criterion may replace a national criterion not only for site-specific concentrations but also for duration of averaging periods and frequencies of allowed exceedances (USEPA, 1983b, 1983c, 1985b). Options that exist for refining site-specific water quality criteria include conducting WER studies, criteria recalculations based on specific organisms that inhabit the specific area of interest, and through the use of the BLM.

USEPA believes that the use of dissolved lead as the basis for establishing water-column criteria for metals may provide more scientifically correct protection. The dissolved lead criteria in this document were developed on this basis, reducing the amount of conservatism that was present in earlier total-recoverable and acid-soluble lead criteria.

7.2   Recalculation of Dissolved Lead Final Acute Value

The acute sensitivities of 34 species range from 73.80 µg/L total lead for *Diaptomus* (copepod) to 1,569,992 µg/L total lead for *Procambarus (*crayfish) (Appendix F). Acute values were converted from dissolved to total lead concentrations because hardness relationships were previously established based on total lead concentrations (Appendix F). The use of total lead values minimized the number of conversions required and helped reduce the uncertainty of the conversion factor in tests reporting acute toxicity with total lead concentrations. Acute toxicity of lead to freshwater animals has shown to decrease as water hardness increases, so a slope factor was calculated. The pooled slope of 1.442 was used to adjust the freshwater acute values to a

hardness (as $CaCO_3$) of 50 mg/L. Additionally, SMAV were recalculated as Genus Mean Acute Values (GMAV) at a hardness of 50 mg/L. Using the procedures described in the *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (USEPA, 1985b), a freshwater FAV for total lead at hardness of 50 mg/L was calculated to be 95.96 µg/L. The total lead FAV was converted to a dissolved lead FAV of 85.60 µg/L using the conversion factor of 0.892.

The new dissolved lead criterion (i.e., 85.60 µg/L) was divided in half, and the criterion maximum intercept was calculated using the following equation:

$$ln(\textbf{Criterion Maximum Intercept}) = ln(X) - [\textbf{pooled slope}*ln(Z)]$$

where: ln = natural log
   X = geometric mean of the values of the water quality characteristic
   Z = selected value of the water quality characteristic

A criterion maximum intercept of -1.884 was calculated, and the freshwater CMC for dissolved lead (µg/L) was determined as follows:

$$e^{(1.442[ln(\textbf{hardness})]-1.884)}$$

where: e = constant
   ln = natural log

Recalculation of Dissolved Lead Final Chronic Value

Acute–chronic ratios were available for six freshwater species, including one fish, one invertebrate, and sensitive species. The geometric mean of the *C. dubia* and *Daphnia magna* Species Mean Acute–Chronic Ratios (SMACRs) yield a freshwater Final Acute–Chronic Ratio (FACR) of 9.299. The Final Chronic Intercept was calculated by dividing the FAV (85.60 µg/L) by the FACR, resulting in 9.206 µg/L dissolved lead (hardness of 50 mg/L). Using the following equation, a final chronic intercept was calculated:

$$ln(\textbf{Final Chronic Intercept}) = ln(X) -[\textbf{pooled slope}*ln(Z)]$$

where: ln = natural log
   X = geometric mean of the values of the water quality characteristic
   Z = selected value of the water quality characteristic

The final chronic intercept was -3.421, and the freshwater CCC for dissolved lead (µg/L) was determined to be the following:

$$e^{(1.442[ln(\textbf{hardness})]-3.421)}$$

where: e = constant
   ln = natural log

7.3   Historical and Recalculated Dissolved Lead Criteria Comparisons

Since 1994, there have been 42 compliance monitoring events at SD8(1) on the north fork of Chollas Creek. Over that period, there have been zero and 19 exceedances based on current dissolved lead CMC and CCC values, respectively. By comparing the new USEPA criteria data to the historical compliance monitoring data, recalculation of the dissolved lead CMC and CCC values resulted in zero and three exceedances, respectively (Figure 7-1). The three dissolved CCC exceedances all occurred prior to November 2001.

Since 2004, there have been 19 compliance monitoring events at Site DPR2 on the south fork of Chollas Creek. Over that period, there have been zero and four exceedances based on current dissolved lead CMC and CCC values, respectively. By comparing the new USEPA criteria data to the historical compliance monitoring data, recalculation of the dissolved lead CMC and CCC values resulted in no exceedances of either standard (Figure 7-2).
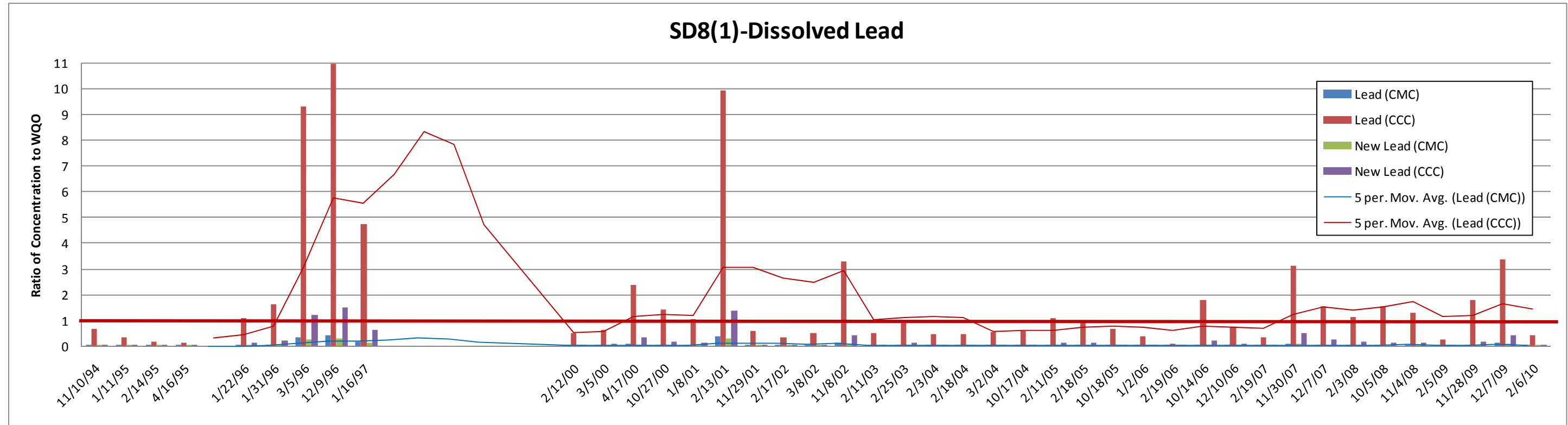
Figure 7-1. Historical and Recalculated Dissolved Lead Exceedance Ratios for Site SD8(1) – North Fork of Chollas Creek
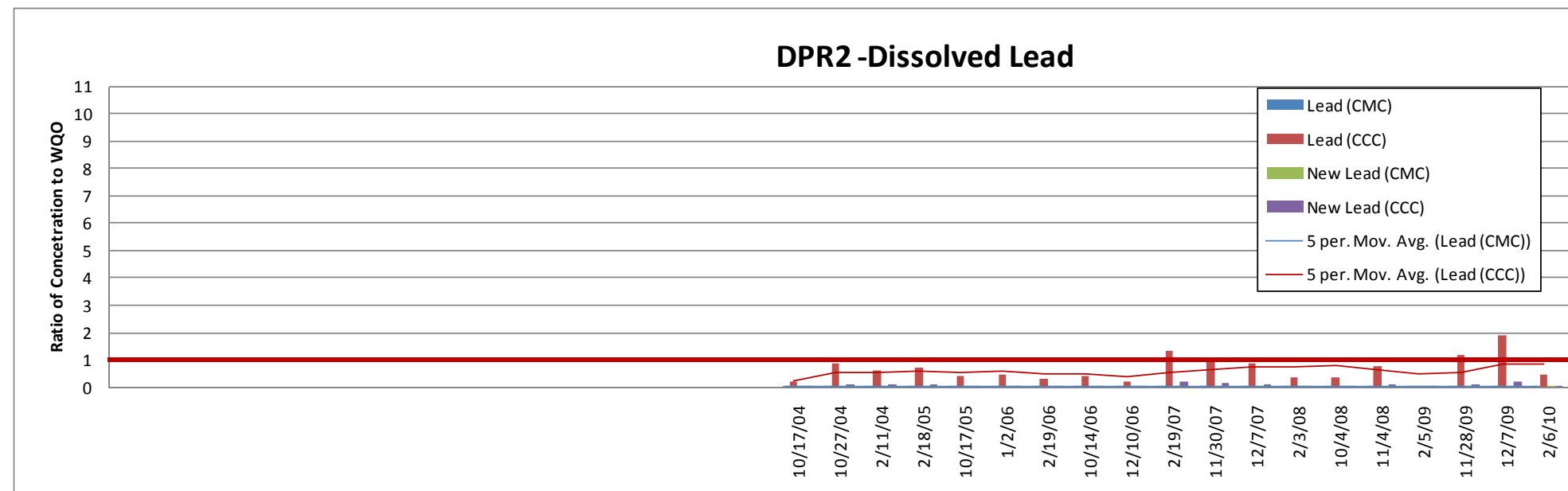
Figure 7-2. Historical and Recalculated Dissolved Lead Exceedance Ratios for Site DPR2 – South Fork of Chollas Creek

8.0   BIOTIC LIGAND MODEL RESULTS

Before performing BLM calculations for the Chollas Creek dataset, the concentration of several necessary model inputs had to be estimated. For DPR2 and SD8(1) Chollas Creek monitoring stations, concentrations for all BLM inputs were available. Dissolved organic carbon inputs for several of the DMW toxicity tests had to be estimated from the DMW DOC concentration measured in the February 2, 2011 sample (Table 8-1). These estimates were inconsequential because BLM calculations for the February 2, 2011 DMW sample were the only ones utilized in this analysis. Several of the necessary inputs for the upstream Chollas Creek stations, Lemon Grove (LG-1) and La Mesa (LM-1), waters were missing and had to be estimated. This resulted in a large amount of uncertainty for the BLM calculations for the November 28, 2009 and February 6, 2010 LG-1 and LM-1 water samples. Since water hardness was measured for these samples, it was assumed that calcium, magnesium, sodium, potassium, sulfate, chlorine, and alkalinity concentrations varied proportionally with hardness on the basis of ratios defined from the October 6, 2010 samples. Unfortunately, DOC measurements were also missing for these waters, so the values for DOC were assumed to be equal to the DOC concentrations provided for the October 6, 2010 samples. Since DOC is an extremely important parameter with respect to BLM calculations, the BLM results for the LG-1 and LM-1 samples from November 28, 2009 and February 6, 2010 should be used with caution. A summary of the BLM inputs used in this analysis is provided in Table 8-1.

Sample results for dissolved copper, lead, zinc, and total hardness were compared for the upstream sites in each fork of Chollas Creek (Figure 8-1). Results are generally similar between the upstream and downstream sites (SD8(1) and LM-1 in the north fork and LG-1 and DPR2 in the south fork). The mean results of each site were within the upper and lower quartiles of the data. These results demonstrate that the application of the WERs developed at the two compliance sites is appropriate for use in assessing sites upstream within the watershed.
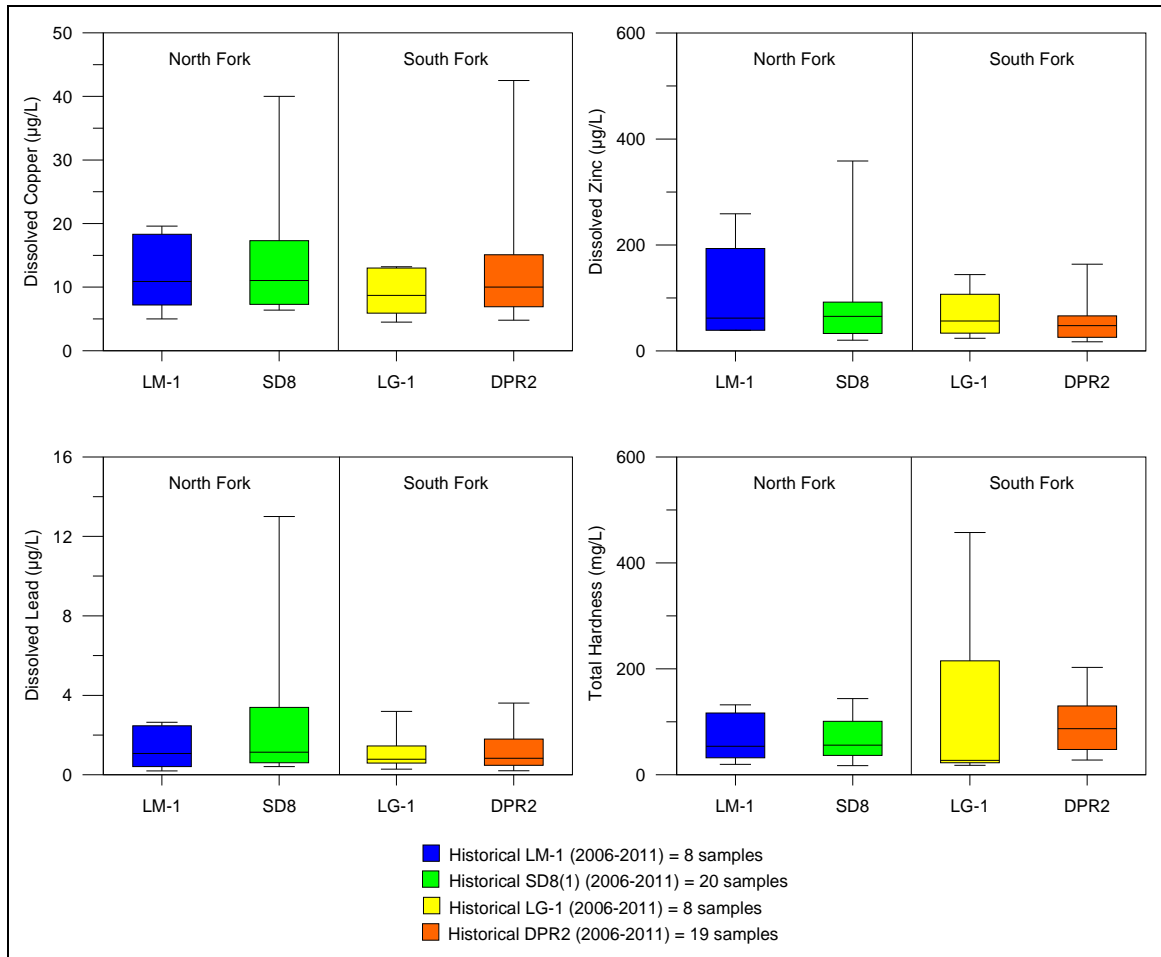
Figure 8-1. Box Whisker Plot of Dissolved Copper, Lead, and Zinc and Total Hardness for Chollas Creek Site Comparison of Upstream Sites

Results of the BLM analyses are shown for each water sample in Table 8-2 (dissolved copper), Table 8-3 (dissolved zinc), and Table 8-4 (dissolved lead). Additional graphical summaries for each site are provided in Figure 8-1 to Figure 8-5. Overall, the BLM-predicted dissolved copper and Zn LC_{50}s for *C. dubia* agree very well with the reported LC_{50}s for the waters tested (i.e., stations DPR2 and SD8(1)) (Figure 8-2 and Figure 8-3). The BLM predictions and reported LC_{50}s show a similar temporal pattern. This temporal pattern in BLM predictions was due to the time-varying water chemistry conditions in the waters tested. The observation that BLM results and toxicity test results were similar and follow a similar temporal pattern suggests that the BLM adequately accounted for the effects of metal bioavailability in the waters tested.

Reported copper concentrations for SD8(1) and DPR2 were generally lower than the BLM-derived CMC and CCC values (Table 8-2 and Figure 8-2 and Figure 8-3). There were three cases where the reported copper concentrations were greater than or equal to the BLM-derived CCC values (i.e., December 20, 2010 for DPR2; October 30, 2010 and December 20, 2010 for

SD8(1)). In all cases, the BLM-derived water quality criteria for all three metals were higher than the hardness-based water quality criteria, although in two cases, the CCC values were similar.

It should be noted that the BLM-derived zinc CMC and CCC values should be considered draft criteria, as the BLM is not a USEPA-approved method for deriving site-specific water quality criteria for zinc. Reported zinc concentrations for SD8(1) and DPR2 were generally below the BLM-derived CMC values and the BLM-derived CCC values (Table 8-3 and Figure 8-2 and Figure 8-3). The one exception occurred for the October 30, 2010 sample for SD8(1), when the reported zinc concentration exceeded the associated CCC. The BLM-derived water quality criteria for zinc were not consistently higher than the hardness-based water quality criteria as observed in the dissolved copper water quality criteria. Regardless, the BLM provides estimates that were consistent with a bioavailability-based approach.

All BLM-predicted LC_{50}s for lead at stations were orders of magnitude greater than the reported lead concentrations for all sites considered (Table 8-4 and Figure 8-2 to Figure 8-5).

Reported lead concentrations were below the BLM-based-WER-adjusted water quality criteria for all sites, in all cases (Table 8-4 and Figure 8-2 and Figure 8-5). The BLM-based lead water quality criteria were always higher than the hardness-based water quality criteria, although in two cases they were similar. This analysis suggests that a BLM-based approach to deriving site-specific water quality criteria in Chollas Creek generally results in higher water quality criteria and fewer exceedances than a hardness-based approach. Caution should be used in interpreting the BLM results for the LG-1 and LM-1 stations for which many of the BLM input parameters were estimated. As a result of this observation, the City has implemented the collection of parameters, where applicable in Chollas Creek (e.g. SD8(1), DPR2, LM-1 and LG-1), that are needed to run the BLM. It should be noted that the BLM is a USEPA-approved method for deriving site-specific water quality criteria for copper, whereas the BLM is not USEPA approved for zinc or lead. The approaches described here for zinc and lead do represent bioavailability-based methods and are consistent with application of the BLM to evaluate the potential for adverse effects on a site-specific basis.

Table 8-1. Inputs Used for Biotic Ligand Model Analysis

(Where there were data for duplicate samples, values were averaged. Values with a "<" designation were entered at half the reported value.)

Sample	Date	pH	DOC	Ca	Mg	Na	K	SO4	Cl	Alkalinity	Hardness	Estimated
							mg/L			as mg CaCO₃/L		
DPR2	27-Feb-10	7.65	8.5	17.5	8.6	43.1	2.5	26.8	63.8	48.0	74.0	
SD8(1)	27-Feb-10	7.51	8.1	11.2	4.2	17.6	2.5	15.0	19.2	32.5	36.6	
DMW	28-Feb-10	8.60	0.46	21.7	8.4	2.5	2.5	3.7	2.0	101.0	85.4	DOC*
SD8(1)	1-Apr-10	7.36	25.15	14.4	4.5	20.8	2.5	19.8	27.8	30.5	49.9	
DPR2	1-Apr-10	7.15	28.5	26.4	10.2	49.2	5.3	35.6	86.7	47.0	103.4	
DMW	2-Apr-10	8.20	0.46	14.2	7.0	0.3	0.3	3.8	2.2	98.0	64.1	DOC*
CC-SD8 (1)	30-Oct-10	7.31	8.2	13.5	4.8	18.0	4.4	17.0	23.0	35.5	52.0	
DPR2	30-Oct-10	7.30	11	24.0	8.2	44.0	3.8	28.0	74.0	66.0	93.0	
DMW	31-Oct-10	8.20	0.46	24.0	8.0	3.2	0.4	3.9	3.0	100.0	81.2	All except pH*
CC-SD8 (1)	20-Dec-10	6.93	3.9	11.0	3.1	13.0	3.0	12.0	15.0	33.0	39.0	
DPR2	20-Dec-10	6.96	4.55	13.0	4.7	22.5	3.2	15.0	35.0	39.0	53.0	
DMW	21-Dec-10	8.50	0.46	24.0	8.0	3.2	0.4	3.9	3.0	100.0	81.2	All except pH*
LG-1	28-Nov-09	7.76	21	96.0	54.9	259.1	11.9	146.3	472.4	152.4	457.2	All except pH**
LM-1	28-Nov-09	7.75	14	22.1	14.7	67.6	3.0	59.0	86.0	49.8	116.7	All except pH**
LG-1	6-Feb-10	8.06	21	5.8	3.3	15.6	0.7	8.8	28.5	9.2	27.6	All except pH**
LM-1	6-Feb-10	8.18	14	9.1	6.1	27.7	1.2	24.2	35.3	20.4	47.9	All except pH**
LG-1	6-Oct-10	7.64	21	63.0	36.0	170.0	7.8	96.0	310.0	100.0	300.0	
LM-1	6-Oct-10	7.87	14	36.0	24.0	110.0	4.9	96.0	140.0	81.0	190.0	
DMW	2-Feb-11	8.20	0.46	24.0	8.0	3.2	0.4	3.9	3.0	100.0	94.0	

*Input values assumed to be equal to those for DMW 2-Feb-11
**Input values assumed to be proportional to Hardness from associated 6-Oct-10 samples; DOC assumed to be equal to values from 6-Oct-10

Table 8-2. Hardness-Based and Biotic Ligand Model -Based Water Quality Criteria for Copper (for Sites within Chollas Creek

(Values shown are median lethal concentrations (LC50), criteria maximum concentrations (CMC), and criteria continuous concentrations (CCC).)

Water Tested*	Date	Hardness (as mg CaCO₃/L)	(µg/L)		Hardness Equation (µg/L)			BLM Results (µg/L)		
			Cu Concentration	Reported LC₅₀	Cu CMC	Cu CCC	LC₅₀	Cu CMC	Cu CCC	
DPR2	27-Feb-10	74	6.5	82.4	10.1	6.9	157.5	51.3	31.9
SD8(1)	27-Feb-10	36.6	7.15	67.6	5.2	3.8	111.5	35.2	21.8
DMW	28-Feb-10	85.4	0.2	5.1	11.6	7.8	20.8	7.1	4.4
SD8(1)	1-Apr-10	49.9	17.2	195.0	7.0	4.9	310.7	97.3	60.4
DPR2	1-Apr-10	103.4	15.1	235.0	13.9	9.2	308.6	95.0	59.0
DMW	2-Apr-10	64.1	0.2	5.2	8.8	6.1	13.4	4.4	2.7
CC-SD8 (1)	30-Oct-10	52	16.5	102.8	7.3	5.1	87.8	27.0	16.8
DPR2	30-Oct-10	93	12	136.2	12.6	8.4	135.2	41.8	26.0
DMW	31-Oct-10	81	0.68	4.6	11.0	7.5	14.8	4.8	3.0
CC-SD8 (1)	20-Dec-10	39	6.4	59.3	5.5	4.0	23.0	6.8	4.2
DPR2	20-Dec-10	53	7	86.7	7.4	5.2	30.2	9.0	5.6
DMW	21-Dec-10	81	0.022	3.8	11.0	7.5	19.4	6.6	4.1
LG-1	28-Nov-09	457	13.2	-	56.3	32.8	655.8	230.9	143.4
LM-1	28-Nov-09	117	19.6	-	15.6	10.2	318.9	107.5	66.8
LG-1	6-Feb-10	28	4.5	-	4.1	3.0	548.9	192.3	119.4
LM-1	6-Feb-10	48	5	-	6.7	4.8	418.5	148.7	92.4
LG-1	6-Oct-10	300	10	-	37.8	22.9	527.1	179.5	111.5
LM-1	6-Oct-10	190	13	-	24.6	15.5	397.0	138.5	86.0
DMW	2-Feb-11	94	-	-	12.7	8.5	14.8	4.8	3.0

*See Table 8-1 for a description of inputs and comments regarding estimates

Table 8-3. Hardness-Based and Biotic Ligand Model-Based Water Quality Criteria for Zinc for Sites Within Chollas Creek

(Values shown are median lethal concentrations (LC$_{50}$), criteria maximum concentrations (CMC), and criteria continuous concentrations (CCC).

Water Tested*	Date	Hardness (as mg CaCO$_3$/L)	(µg/L)			Hardness Equation (µg/L)			BLM Results (µg/L)		
			Zn Concentration	Reported LC$_{50}$		Zn CMC	Zn CCC		LC$_{50}$	Zn CMC	Zn CCC
DPR2	27-Feb-10	74	19.1	262.7		90.8	91.5		402.0	218.8	82.1
SD8(1)	27-Feb-10	36.6	21.15	155.3		50.0	50.4		323.5	176.0	66.1
DMW	28-Feb-10	85.4	0.05	178.9		102.5	103.4		306.9	175.4	65.9
SD8(1)	1-Apr-10	49.9	76.15	395.6		65.0	65.6		837.0	453.5	170.3
DPR2	1-Apr-10	103.4	66.2	508.1		120.5	121.5		876.9	479.3	180.0
DMW	2-Apr-10	64.1	0.11	153.7		80.4	81.0		157.3	89.6	33.6
CC-SD8 (1)	30-Oct-10	52	75.5	349.8		67.3	67.9		300.9	165.0	62.0
DPR2	30-Oct-10	93	37	313.1		110.2	111.1		441.6	242.8	91.2
DMW	31-Oct-10	81	2.2	262.3		98.0	98.8		207.1	118.2	44.4
CC-SD8 (1)	20-Dec-10	39	26	153.8		52.8	53.2		142.4	80.0	30.0
DPR2	20-Dec-10	53	21	198.0		68.4	69.0		168.8	94.7	35.5
DMW	21-Dec-10	81	0.3	177.0		98.0	98.8		277.9	158.8	59.6
LG-1	28-Nov-09	457	144	-		424.6	428.1		1602.7	878.8	330.0
LM-1	28-Nov-09	117	193.4	-		133.9	134.9		684.0	369.5	138.7
LG-1	6-Feb-10	28	23.9	-		39.9	40.2		1058.0	561.7	210.9
LM-1	6-Feb-10	48	38.9	-		62.9	63.4		757.9	403.1	151.4
LG-1	6-Oct-10	300	60	-		297.2	299.7		1246.3	678.4	254.7
LM-1	6-Oct-10	190	68	-		201.9	203.5		868.4	470.8	176.8
DMW	2-Feb-11	94	-	-		111.2	112.1		208.2	118.8	44.6

*See Table 8-1 for a description of inputs and comments regarding estimates

Table 8-4. Hardness-Based and Biotic Ligand Model -Based Water Quality Criteria for Lead for Sites Within Chollas Creek.

(Values shown are median lethal concentrations (LC50), criteria maximum concentrations (CMC), criteria continuous concentrations (CCC).), and BLM-derived water effect ratios (WER).)

Water Tested*	Date	Hardness (as mg CaCO$_3$/L)	(µg/L)		Hardness Equation (µg/L)		BLM Results (µg/L)			
			Pb Concentration	Reported LC$_{50}$	Pb CMC	Pb CCC	LC$_{50}$	WER**	Pb CMC***	Pb CCC***
DPR2	27-Feb-10	74	0.89	-	46.5	1.8	1096.3	4.6	214.5	8.4
SD8(1)	27-Feb-10	36.6	1.325	-	21.3	0.8	835.8	3.5	74.9	2.9
DMW	28-Feb-10	85.4	0.1	-	54.4	2.1	250.7	1.1	57.4	2.2
SD8(1)	1-Apr-10	49.9	2.065	-	30.1	1.2	2467.8	10.4	312.5	12.2
DPR2	1-Apr-10	103.4	1.24	-	67.0	2.6	2882.2	12.1	812.9	31.7
DMW	2-Apr-10	64.1	0.11	-	39.7	1.5	156.7	0.7	26.2	1.0
CC-SD8 (1)	30-Oct-10	52	0.615	-	31.5	1.2	772.6	3.3	102.4	4.0
DPR2	30-Oct-10	93	0.59	-	59.7	2.3	1230.8	5.2	309.3	12.1
DMW	31-Oct-10	81	0.024	-	51.3	2.0	232.9	1.0	50.3	2.0
CC-SD8 (1)	20-Dec-10	39	0.51	-	22.9	0.9	256.7	1.1	24.7	1.0
DPR2	20-Dec-10	53	0.49	-	32.1	1.3	334.8	1.4	45.3	1.8
DMW	21-Dec-10	81	0.017	-	51.3	2.0	262.5	1.1	56.7	2.2
LG-1	28-Nov-09	457	3.19	-	321.8	12.5	4517.0	19.0	6121.2	238.5
LM-1	28-Nov-09	117	2.64	-	76.6	3.0	2029.7	8.5	654.7	25.5
LG-1	6-Feb-10	28	0.67	-	15.8	0.6	2505.0	10.5	166.4	6.5
LM-1	6-Feb-10	48	2.47	-	28.8	1.1	1949.5	8.2	236.5	9.2
LG-1	6-Oct-10	300	0.84	-	208.6	8.1	3771.0	15.9	3312.6	129.1
LM-1	6-Oct-10	190	0.41	-	128.9	5.0	2527.8	10.6	1372.4	53.5
DMW	2-Feb-11	94	-	-	60.4	2.4	237.5	1.0	60.4	2.4

*See Table 8-1 for a description of inputs and comments regarding estimates
**BLM-calculated Water Effect Ratio (WER) was based upon predicted toxicity in each water tested/predicted toxicity in the DMW sample from 2-Feb-11
***BLM-calculated CMC and CMC values represent the product of the hardness-based criteria values and the BLM-calculated WER
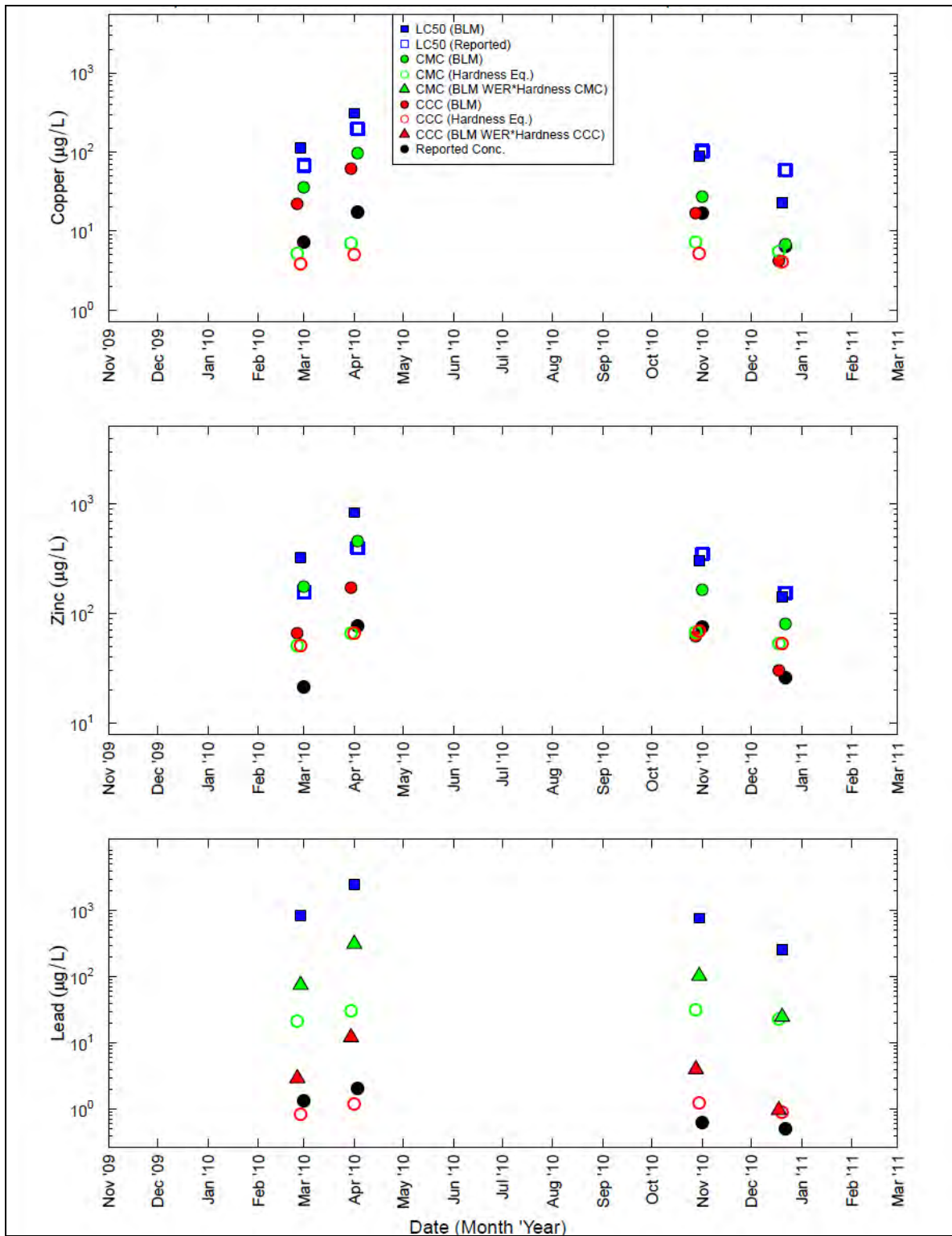
Figure 8-2. Comparison of Measured Dissolved Metal Concentrations, Toxicological Effects Levels, Water Quality Criteria, and BLM Predictions for Station SD8(1), Chollas Creek North Fork

Figure 8-3. Comparison of Measured Dissolved Metal Concentrations, Toxicological Effects Levels, Water Quality Criteria, and BLM Predictions for Station DPR2, Chollas Creek South Fork

Figure 8-4. Comparison of Measured Dissolved Metal Concentrations, Toxicological Effects Levels, Water Quality Criteria, and BLM Predictions for Station LM-1, Chollas Creek North Fork
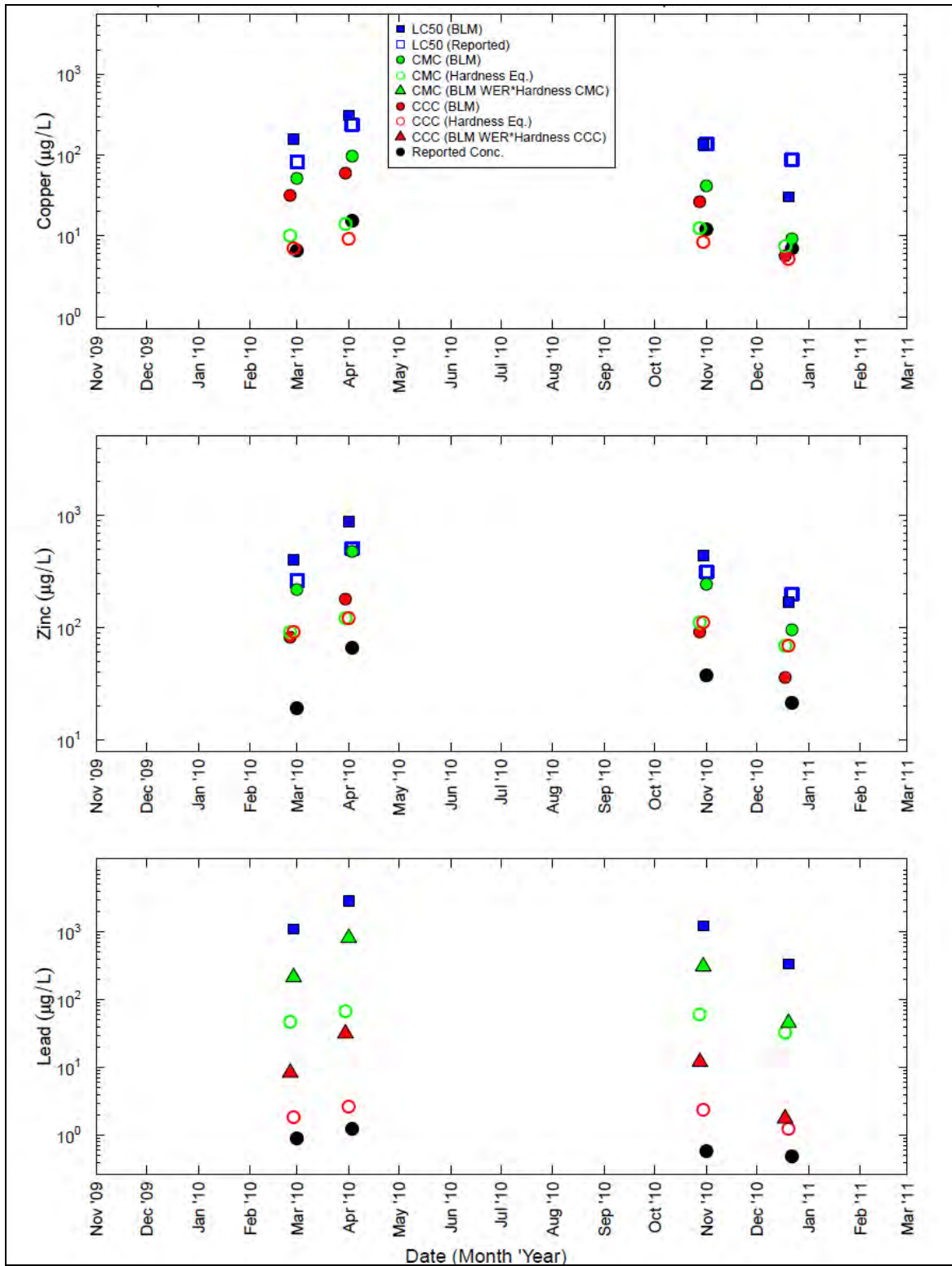
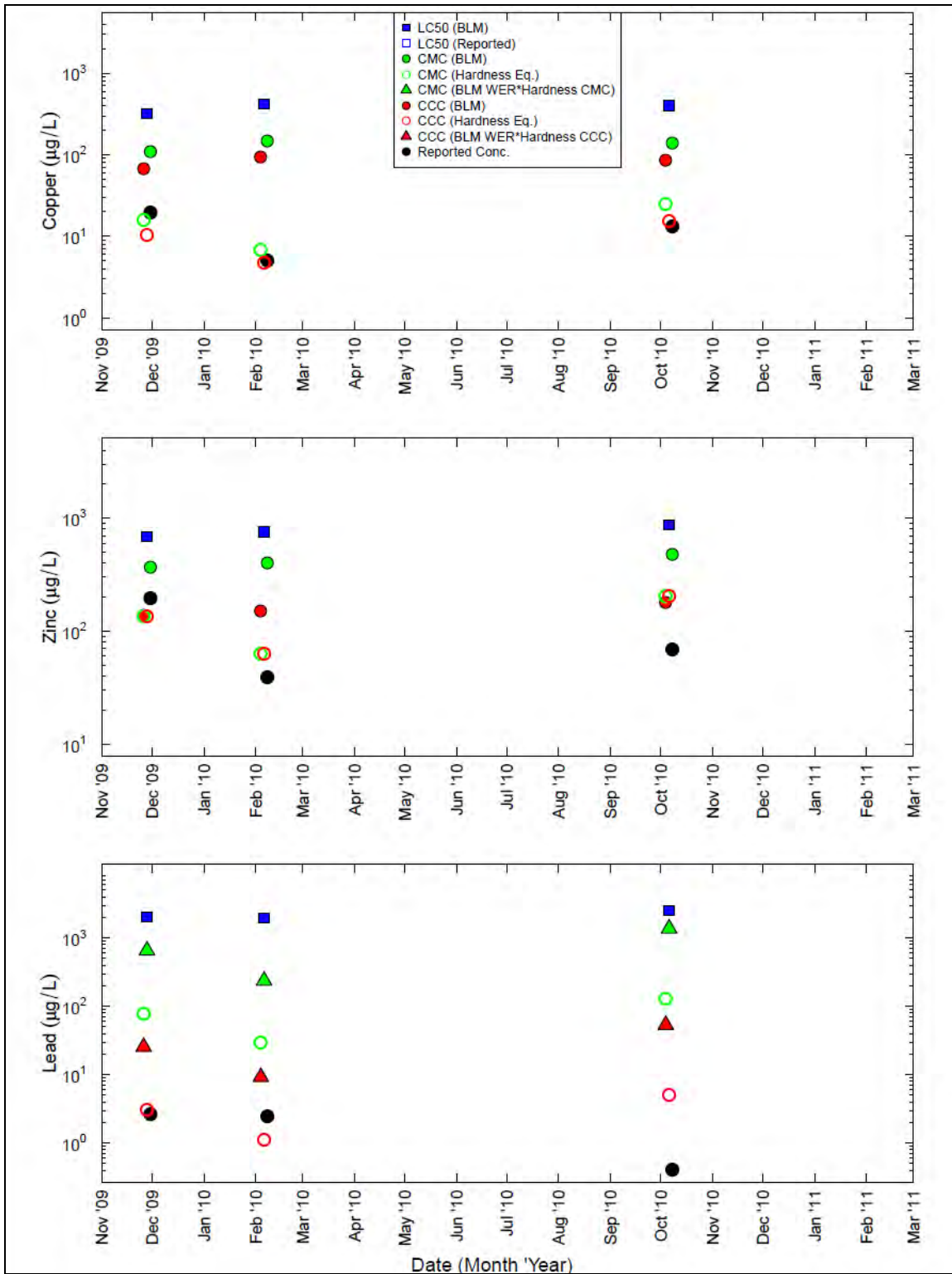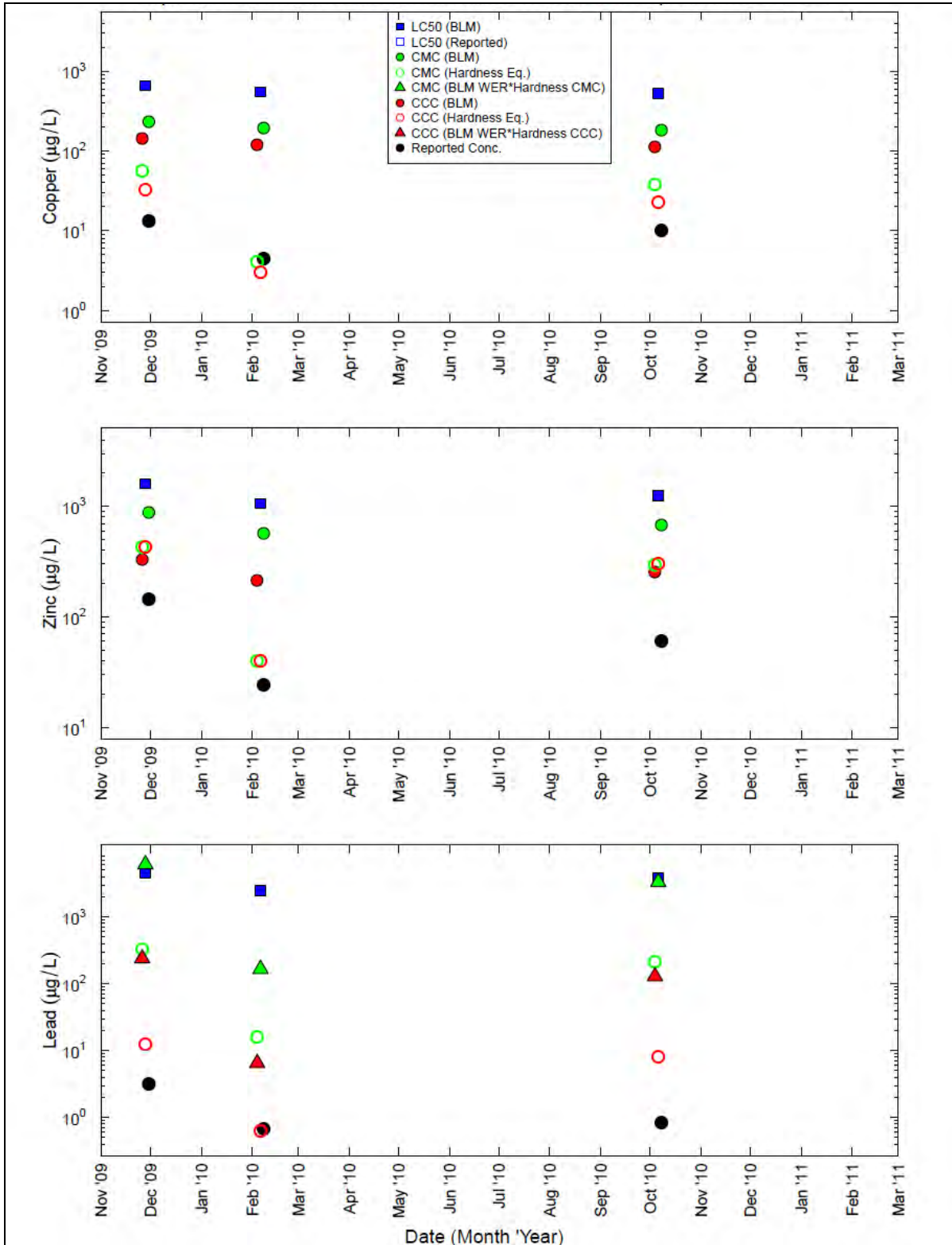**Figure 8-5. Comparison of Measured Dissolved Metal Concentrations, Toxicological Effects Levels, Water Quality Criteria, and BLM Predictions for Station LG-1, Chollas Creek South Fork**

9.0   SUMMARY AND RECOMMENDATIONS

9.1   Summary

Based on the final results of the WER, the following summary can be made:

Dissolved Copper:

- Site SD8(1), north fork, dissolved copper WERs for 48-hour *C. dubia* toxicity experiments were 6.40, 3.06, 8.82, 4.65, and 2.68 for samples collected on January 18, 2010; February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010, respectively.

- The geometric mean (±standard deviation) of the five individual WERs for the north fork of Chollas Creek (i.e., SD8(1)) was 4.64 (2.54).

- Site DPR2 dissolved copper WERs for 48-hour *C. dubia* toxicity experiments were 3.73, 10.63, 6.16, and 3.92 for samples collected on February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010, respectively.

- The geometric mean (±standard deviation) of the four individual WERs for the south fork of Chollas Creek (i.e., DPR2) was 5.56 (3.21).

- The recommended conservative final WER for dissolved copper is 4.64, if one value can be used for both forks of Chollas Creek.

Dissolved Zinc:

- Site SD8(1) dissolved zinc WERs for 48-hour *C. dubia* toxicity experiments were 2.1, 0.9, 2.6, 1.3, and 0.9 for samples collected on January 18, 2010; February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010, respectively.

- The geometric mean (±standard deviation) of the five individual WERs for the north fork of Chollas Creek (i.e., SD8(1)) was 1.4 (0.76).

- Site DPR2, south fork, dissolved zinc WERs for 48-hour *C. dubia* toxicity experiments were 1.5, 3.3, 1.2, and 1.1 for samples collected on February 27, 2010; April 1, 2010; October 30, 2010; and December 20, 2010, respectively.

- The geometric mean (±standard deviation) of the four individual WERs for the south fork of Chollas Creek (i.e., DPR2) was 1.6 (1.04).

- The recommended conservative final WER for dissolved zinc is 1.40, if one value can be used for both forks of Chollas Creek.

Dissolved Lead:

- Based on recently available USEPA lead toxicity curves, a revised freshwater FAV for total lead at a hardness of 50 mg/L was calculated to be 95.96 µg/L. The total lead FAV was converted using the conversion factor 0.892 to a new dissolved lead FAV of 85.60µg/L.

- A new freshwater criterion maximum concentration (CMC or Acute) for dissolved lead (µg/L) was developed, as follows:

$$e^{(1.442[ln(\text{hardness})]-1.884)}$$

> where: *e* = constant
> *ln* = natural log

- A new freshwater criterion continuous concentration (CCC or Chronic) for dissolved lead (µg/L) was developed, as follows:

$$e^{(1.442[ln(\text{hardness})]-3.421)}$$

> where: *e* = constant
> *ln* = natural log

Compliance Comparison:

- Based on the study data collected to date, the historical compliance results for Site SD8(1) in the north fork were re-evaluated to compare the number of exceedances using existing criteria to occurrences using the newly obtained criteria (Table 9-1). Results show that exceedances were limited to two occurrences of dissolved copper (one acute and chronic, and one chronic only), nine occurrences for dissolved zinc (acute and chronic), and three occurrences for dissolved lead (chronic only).

- Based on the study data collected to date, the historical compliance results for Site DPR2 in the south fork were re-evaluated to compare the number of exceedances using existing criteria to occurrences using the newly obtained criteria (Table 9-2). Results show that there were no exceedances of either the CMC or CCC for any of the three dissolved metals.

Table 9-1. Dissolved Copper, Lead, and Zinc Acute and Chronic Historical Exceedances Compared to Exceedances After Site-Specific Adjustments Applied at Site SD8(1)

Dissolved CMC (Acute)	Total Exceedances Using Current Criteria (n=45)	Total Exceedances with WER (Cu = 4.64, Zn = 1.4) and Recalc for Lead (n=45)*
Copper	23	1
Lead	0	0
Zinc	15	9

Dissolved CCC (Chronic)	Total Exceedances Using Current Criteria (n=45)	Total Exceedances with WER (Cu = 4.64, Zn = 1.4) and Recalc for Lead (n=45)*
Copper	31	2
Lead	19	3
Zinc	15	9
*WER is based on most conservative value calculated to date. Lead is based on draft revised lead criteria.		

Table 9-2. Dissolved Copper, Lead, and Zinc Acute and Chronic Historical Exceedances Compared to Exceedances After Site-Specific Adjustments Applied at Site DPR2

Dissolved CMC (Acute)	Total Exceedances Using Current Criteria (n=22)	Total Exceedances with WER (Cu = 5.56, Zn = 1.6) and Recalc for Lead (n=22)*
Copper	7	0
Lead	0	0
Zinc	0	0

Dissolved CCC (Chronic)	Total Exceedances Using Current Criteria (n=22)	Total Exceedances with WER (Cu = 5.56, Zn = 1.6) and Recalc for Lead (n=22)*
Copper	16	0
Lead	4	0
Zinc	0	0
*WER is based on most conservative value calculated to date. Lead is based on draft revised lead criteria.		

Biotic Ligand Model

- The BLM was used as a secondary method to verify the biological responses observed during the WER experiments. However, it should be noted that the BLM-predicted zinc and lead CMCs and CCCs should be considered "draft" criteria, as the BLM is not yet a USEPA-approved method for zinc and lead.

- The results of the BLM corroborated the results of the WER study indicating that the current Waste Load Allocations using the default hardness-based CTR formulas are currently over protective.

- For both DPR2 and SD8(1), BLM-predicted LC_{50}s for dissolved copper and dissolved zinc were consistent with measured LC_{50}s.

- BLM predictions for DPR2 and SD8(1) LC_{50}s for *C. dubia* exposed to dissolved copper and zinc and reported LC_{50}s show a similar temporal pattern. This temporal pattern in BLM predictions may be due to the time-varying water chemistry conditions in the waters tested. The observation that BLM results and toxicity test results were comparable and follow a similar temporal pattern, suggests that the BLM adequately accounts for bioavailability effects in the waters tested.

- Reported zinc concentrations for DPR2 and SD8(1) were always below the BLM-predicted CMCs and the BLM-predicted CCCs (i.e., there are no exceedances of water quality criteria for dissolved zinc for either station).

- Reported copper concentrations for DPR2 and SD8(1) were always below the BLM-predicted CMCs, but reported concentrations were greater than or equal to the BLM-predicted CCC in three cases (i.e., December 20, 2010 for DPR2; October 30, 2010 and December 20, 2010 for SD8(1)).

- All BLM-predicted LC_{50}s for lead were orders of magnitude greater than the reported lead concentrations for DPR2 and SD8(1).

- Similar trends were observed in both La Mesa and Lemon Grove for all three dissolved metals compared to SD8(1) and DPR2, respectively. However, the BLM-predicted water quality criteria was greater (i.e., less conservative) by 2-4 X in the upstream stations than the water quality criteria predicted or measured for the downstream stations, indicating greater site-specific protection to aquatic beneficial uses.

Evaluation of Results

- Based on the study data collected to date, historical compliance results for both sites were re-evaluated to compare the number of exceedances from existing criteria to the new site-specific criteria. Results showed that exceedances were greatly reduced when incorporating the newly developed WERs and that the current TMDL criteria are overprotective.

- Based on the re-calculation and comparison to historical results, there were no exceedances in the South Fork site DPR2 for any metal. In the North Fork, there were two exceedances of copper, nine dissolved zinc exceedances and three exceedances of dissolved lead.

- Toxicity test results also corroborate the findings of the WER tests, which indicate that toxicity to *Ceriodaphnia dubia* is no longer a persistent issue as a result of the USEPA ban on the pesticide Diazinon in 2005 (suggesting metals were not a significant factor in the observed toxicity).

9.2   Recommendations

- The WERs measured in these experiments and the revised lead criteria should be incorporated into the TMDL for Chollas Creek through a Basin Plan amendment. These values present scientifically based site-specific objectives that are protective of beneficial uses following the recommendations of the California Toxics Rule for metals criteria.

- In order to add a layer of conservatism, WESTON recommends use of the SD8(1) final WER for development of site-specific objectives for both forks of the watershed: 4.64 for dissolved copper and 1.4 for dissolved zinc.

- Future evaluation of TMDL compliance within the Chollas Creek watershed should incorporate these WERs and the revised lead criteria to evaluate their compliance with site-specific WQOs as shown in Table 9-3.

Table 9-3. Recommended Numeric Targets for Specified Metals in the Chollas Creek Watershed

Criteria	Dissolved Copper	Dissolved Lead	Dissolved Zinc
TMDL WLA-CMC (Acute)	*(4.64) * (0.96) * {e^[(0.9422 * ln hardness)-1.700]}*0.9*	*{e^(1.442[ln(hardness)]-1.884)}*0.9*	(1.44) * (0.978) * {*e*^[(0.8473 * *ln* hardness) + 0.884]}*0.9
TMDL WLA-CCC (Chronic)	*(4.64) * (0.96) * {e^[(0.8545 * ln hardness)-1.702]}*0.9*	*{e^(1.442[ln(hardness)]-3.421)}0.9*	(1.44) * (0.986) * {*e*^[(0.8473* *ln* hardnes*s*) + 0.884]}*0.9

The natural log and exponential functions are represented as "ln" and "e", respectively.

- Periodic confirmation of the WERs is recommended every five years or after a significant change in the watershed's land-use distribution, a significant implementation of BMPs that may alter discharge characteristics and/or alter watershed hydrodynamics, or in the event toxicity patterns warrant follow-up testing.

10.0   REFERENCES

American Public Health Association (APHA). 1998. Standard Methods for the Examination of Water and Wastewater. 19th ed. Washington, D.C. 1325 pp.

Besser, J. M., W. G. Brumbaugh, E. L. Brunson and C. G. Ingersoll. 2005. Acute and Chronic Toxicity of Lead in Water and Diet to the Amphipod *Hyalella azteca*. Environmental Toxicology and Chemistry. 24(7): 1807-1815.

Boenigk, J., A. Wiedlroither and K. Pfandl. 2004 . Heavy Metal Toxicity and Bioavailability of Dissolved Nutrients to a Bacterivorous Flagellate are Linked to Suspended Particle Physical Properties. Aquatic Toxicology.71(3): 249-259.

California Department of Pesticide Regulation, 2004. http://www.cdpr.ca.gov/. Sacramento, California.

California Department of Transportation (Caltrans), 2003. A Review of the Contaminants and Toxicity Associated with Particles in Stormwater Runoff. Caltrans Report# CTSW-RT-03-059.73.15. August, 2003.

California Department of Transportation (Caltrans), 2005. First Flush Phenomenon Characterization. Caltrans Report# CTSW-RT-05-73-02.6. August, 2005.

California Regional Water Quality Control Board, San Diego Region (Regional Board). 2007. Total Maximum Daily Loads for Dissolved Copper, Lead, and Zinc in Chollas Creek, Tributary to San Diego Bay Chollas Creek Watershed. Technical Report. May.

California State Water Resources Control Board (State Board), 2002. 2002 Clean Water Act Section 303(d) List of Water Quality Limited Segments. Accessed at: http://www.waterboards.ca.gov/water_issues/programs/tmdl/303d_lists.shtml

Carroll, J.J., S.J. Ellis and W.S. Oliver. 1979. Influences of Hardness Constituents on the Acute Toxicity of Cadmium to Brook Trout (*Salvelinus fontinalis*). Bulletin. Environ. Contam. Toxicol. 22:575-581.

Carlson, A.R., Nelson, H., and Hammermeister, D. 1986. Development and Validation of Site-Specfiic Water Quality Criteria for Copper. Environmental Toxicology and Chemistry, 5:997-1012.

CH2M Hill. 2002. Boise City Water-Effect Ratio Project. Prepared for: Boise City, Boise, Idaho. August.

City of San Diego. 2010. City Wide Assessment of Synthetic Pyrethroids. Prepared by Weston Solutions, Inc. City of San Diego, CA. June, 2010.

City of San Jose. 1998. Development of a Site-specific Water Quality Criterion for Copper in South San Francisco Bay. Prepared by the Environmental Services Department, City of San Jose, CA. May.

Chapman, G.A., et al., Manuscript. Effects of Water Hardness on the Toxicity of Metals to *Daphnia magna*. U.S. EPA, Corvallis, Oregon.

De Schamphelaere, K.A.C., Heijerick, D.G., Janssen, C.R. 2002. Refinement and field validation of a biotic ligand model predicting acute copper toxicity to *Daphnia magna*. Comparative Biochemistry and Physiology Part *C* 133:243-258.

De Schamphelaere, K.A.C., Janssen, C.R. 2002. A biotic ligand model predicting acute copper toxicity for *Daphnia magna*: the effects of calcium, magnesium, sodium, potassium, and pH. Environmental Science and Technology 36:48-54.

Diamond, J.M., Gerardi, C., Leppo, E., and Miorelli, T. 1997. Using a water-effect ratio approach to establish effects of an effluent-influenced stream on copper toxicity to the fathead minnow. Environmental Toxicology and Chemistry, 16:1480-1487.

Diamond, J.M., Koplish, D.E., McMahon III, J., and Rost, R. 1997b. Evaluation of the water-effect ratio procedure for metals in a riverine system. Environmental Toxicology and Chemistry, 16:509-520.

Di Toro, D.M., Allen, H.E., Bergman. H.L., Meyer, J.S., Paquin, P.R., Santore, R.C. 2001. A biotic ligand model of the acute toxicity of metals I. Technical basis. Environ Toxicol Chem 20:2383-2396.

Earley, P.J., Rosen, G., Rivera-Duarte, I., Gauthier, R.D., Arias-Thode, Y., Thompson, J., Swope, B. 2007. A Comprehensive Copper Compliance Strategy: Implementing Regulatory Guidance at Pearl Harbor Naval Shipyard & Intermediate Maintenance Facility. SPAWAR Systems Center San Diego. Technical Document 1952 (January). San Diego, CA.

Evans, D.H. 1987. The Fish Gill: Site of Action and Model for Toxic Effects of Environmental Pollutants. Environ. Health Perspect. 71:47-58.

Heijerick, D.G., De Schamphelaere, K.A.C., Janssen, C.R. 2002. Predicting acute zinc toxicity for *Daphnia magna* as a function of key water chemistry characteristics: development and validation of a biotic ligand model. Environmental Toxicology and Chemistry 21:1309-1315.

HDR|HydroQual. 2011. Update on progress to date on the phase II biotic ligand model (BLM) development effort for lead. Prepared by HDR|HydroQual, Inc. for the International Lead Zinc Research Organization. February 18, 2011.

HydroQual. 2006. Development of an approach for setting regulatory limits in freshwater with the Zn BLM. Prepared by HydroQual, Inc. for the International Lead Zinc Research Organization. July 3, 2006.

Larry Walker Associates (LWA). 2006. Calleguas Creek Watershed Copper Water-Effect Ratio (WER) Study. June 8.

Larry Walker Associates (LWA). 2008. Los Angeles River Copper Water-Effect Ratio (WER) Study. June 3.

Morel, F.M.M. and J.G. Hering. 1993. Principals and Applications of Aquatic Chemistry. J. Wiley, NewYork. 588 pp.

Nautilus Environmental. 2005. Water and sediment quality evaluation of the Santa Clara River Estuary: analysis of impacts associated with discharge of treated wastewater. Conducted for the City of Buenaventura, CA. Available online at: http://www.nautilusenvironmental.com/images%5CSetac%5CBuenaventura%20Tox.ppt

Pagenkopf, G.K. 1983. Gill Surface Interaction Model for Trace-metal Toxicity to Fishes: Role of Complexation, pH and Water Hardness. Environ. Sci. Technol. 17: 342-347.

Paquin, P.R., Gorsuch, J.W., Apte, S., Batley, G.E., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M., Dwyer, R.L., Galvez, F., Gensemer, R.W., Goss, G.G., Hogstrand. C., Janssen, C.R., McGeer, J.C., Naddy, R.B., Playle, R.C., Santore, R.C., Schneider, U., Stubblefield, W.A., Wood, C.M., Wu, K.B. 2002. The biotic ligand model: a historical overview. Comparative Biochemistry and Physiology Part C 133:3-35.

Rose, W.L., Moore, D.W., and Renfrew, D.S. 2007. The use of toxicity identification evaluations to determine the causative agents of toxicity in storm water samples from the San Diego Region. Recent Findings and Implications. Stormcon '07 Conference Proceedings. Forester Press.

Rosen, Rivera-Duarte, I, Kear-Padilla, L. Chadwick, D.B. 2005. Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper in San Diego Bay, California, USA. Environmental Toxicology and Chemistry, 24:415-422.

Santore, R.C., Di Toro, D.M., Paquin, P.R., Allen, H.E., Meyer, J.S. 2001. A biotic ligand model of the acute toxicity of metals. II. Application to acute copper toxicity in freshwater fish and *Daphnia*. Environ Toxicol Chem 20:2397-2402.

S. R. Hansen & Associates. 1992. Development of site-specific criteria for copper for San Francisco Bay. Prepared for the San Francisco Regional Water Quality Control Board, Oakland, CA.

Stephan, C.E., Mount, D.I., Hanson, D.J., Gentile, J.H., Chapman, G.A., Brungs, W.A. 1985. Guidelines for Deriving Numeric National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses. PB85-227049. Environmental Protection Agency, Duluth, Minnesota.

Tidepool Scientific Software. ToxCalc™ v1.1.2 rev H 5.0. McKinley, CA.

U.S. EPA. 1983a. Methods for chemical analysis of water and wastes. EPA-600/4-79-020 (Revised March 1983). National Technical Information Service, Springfield, Virginia.

U.S. EPA. 1983b. Water quality standards regulation. Federal Register 48:51400. November 8.

U.S. EPA. 1983c. Water quality standards handbook. Office of Water Regulations and Standards, Washington, D.C.

U.S. EPA. 1985a. Ambient water quality criteria for lead. EPA-440/5-84-027 (Revised late 1984). National Technical Information Service, Springfield, Virginia.

United States Environmental Protection Agency (USEPA). 1985b. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses.

U.S. EPA. 1987. Permit writers guide to water quality-based permitting for toxic pollutants. EPA-440/4-87-005. Office of Water, Washington, DC.

U.S. EPA. 1991. Technical support document for water quality-based toxics control. EPA-505/2-90-001. Office of Water, Washington, DC, March; or PB91-127415, National Technical Information Service, Springfield, VA.

United States Environmental Protection Agency (USEPA). 1992. Synopsis of water-effect ratios for heavy metals as derived for site-specific water quality criteria. Prepared under USEPA Contract No. 68- C0-0070. March.

United States Environmental Protection Agency (USEPA). 1994. Interim Guidance on Determination and Use of Water-Effect Ratios for Metals. EPA-823-B-94-001. February.

United States Environmental Protection Agency (USEPA). 1997. Modifications to Guidance Site-Specific Criteria. Health and Ecological Criteria Division, Office of Water. December.

United States Environmental Protection Agency (USEPA). 2001. Streamlined Water-Effect Ratio Procedure for Discharges of Copper. EPA 822-R-01-005.

United States Environmental Protection Agency (USEPA). 2002a. California Toxics Rule. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Federal Registry Rule – 40 CFR Part 131. May 28, 2002.

United States Environmental Protection Agency (USEPA). 2002b. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Fifth Edition. EPA-821-R-02-012. October.

United States Environmental Protection Agency (USEPA). 2007. Aquatic Life Ambient Freshwater Quality Criteria – Copper. 2007 Revision. United States Environmental Protection Agency, Office of Water, Washington, DC. EPA 822-R-07-001, February 2007.

United States Environmental Protection Agency (USEPA). 2008. Aquatic Life Criteria for Lead Website. References Available to USEPA for Developing or Revising Aquatic Life Criteria for Lead. (Accessed June 2009 at (http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/pollutants/lead/index.cfm)

Wheelock, C.E., Miller, J.L., Miller, M.J., Phillips, B.M., Gee, S.J., Tjeerdema, R.S., and B.D. Hammock. 2005. Influence of container adsorption upon observed pyrethroid toxicity to *Ceriodaphnia dubia* and *Hyalella azteca*. Aquatic Toxicology, 74:47-52.

Wheelock, C.E., Miller, J.L., Miller, M.J., Phillips, B.M., Gee, S.J., Tjeerdema, R.S., and B.D. Hammock. 2005. Influence of container adsorption upon observed pyrethroid toxicity to *Ceriodaphnia dubia* and *Hyalella azteca*. Aquatic Toxicology, 74:47-52.

WESTON (Weston Solutions, Inc.). 2007. *San Diego County Municipal Copermittees 2005– 2006 Receiving Waters and Urban Runoff Monitoring Report*. Prepared for the County of San Diego. January 2007.

Zar, J. H. 1999. Biostatistical Analysis. Fourth Edition. Upper Saddle River, NJ: Prentice Hall.