

**WORK PLAN FOR COPPER AND NICKEL IMPAIRMENT
ASSESSMENT TO ASSIST IN PREPARATION OF 2002 303(d) LIST**

SAN FRANCISCO BAY NORTH OF DUMBARTON BRIDGE

Prepared for

**North Bay Dischargers Group
Bay Area Dischargers Association
Western States Petroleum Association**

Prepared by

**Thomas R. Grovhoug, LWA
Samantha Salvia, EOA**

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INTRODUCTION.....	3
ISSUES	3
PURPOSE	4
OBJECTIVES	4
BACKGROUND	4
PRIOR STUDIES IN SAN FRANCISCO BAY	4
KEY FINDINGS OF PRIOR STUDIES	5
AMBIENT DATA FOR SAN FRANCISCO BAY	7
MODELING RESULTS	8
LIMITATIONS OF EXISTING INFORMATION	8
HYPOTHESES.....	8
PROPOSED APPROACH	9
COPPER	9
NICKEL	11
GENERAL DESCRIPTION OF WORK.....	11
SAMPLING LOCATIONS.....	11
SAMPLING PERIOD	13
METHODOLOGY	14
<i>Water Collection</i>	<i>14</i>
<i>Site Water Preparation and Salinity Adjustment.....</i>	<i>14</i>
<i>Laboratory water.....</i>	<i>15</i>
<i>Toxicity Testing Procedure</i>	<i>15</i>
<i>Chemical Analyses</i>	<i>16</i>
<i>Secondary Testing</i>	<i>16</i>
<i>QA/QC.....</i>	<i>16</i>
PROGRAM MANAGEMENT	17
<i>Administration.....</i>	<i>17</i>
<i>Data Analysis</i>	<i>17</i>
<i>Reporting.....</i>	<i>17</i>
<i>External Review.....</i>	<i>17</i>
<i>Stakeholder Outreach.....</i>	<i>18</i>
<i>Regulatory Liaison.....</i>	<i>18</i>
<i>Program Manager.....</i>	<i>18</i>
<i>Estimated Costs</i>	<i>18</i>
REFERENCES.....	20

TABLE 1 RMP Sampling Constituents

TABLE 2 Sample Stations and Locations

TABLE 3 Summary Of Estimated Costs For Proposed WER Testing And Chemical Analysis

FIGURE 1 Impairment Assessment Monitoring

APPENDIX A - RMP Data Summaries

APPENDIX B – Hydrodynamic Modeling Results

INTRODUCTION

In accordance with Section 303(d) of the Clean Water Act, States are required to list waters that will not comply with adopted water quality objectives after imposition of technology-based controls on point source discharges. San Francisco Bay was listed on the 1998 303(d) list for California due to levels of copper and nickel which exceeded 1986 Basin Plan objectives and/or USEPA national criteria. These exceedances were the basis for a concern that copper and nickel were impairing aquatic uses in the Bay by producing either acute or chronic toxicity in sensitive aquatic organisms.

However, the actual bioavailability and toxicity of certain compounds can vary from water body to water body due to differences in factors such as pH, hardness, suspended solids, dissolved carbon compounds, salinity, and other constituents. Recent studies of the San Francisco Bay, including work performed by the City of San Jose and RMP data from 1993 through 1998 suggest that the Bay may not be impaired by ambient levels of copper and nickel. The State will soon be preparing its 303(d) list for 2002. This purpose of this workplan is to gather data necessary to assess impairment of the San Francisco Bay north of the Dumbarton Bridge, for copper and nickel, and to evaluate whether the San Francisco Bay north of the Dumbarton Bridge should remain on the 303(d) list for copper and nickel.

ISSUES

Extensive work completed by the City of San Jose in Lower South San Francisco Bay (south of the Dumbarton Bridge) has indicated that the toxicity of copper and nickel to sensitive aquatic species in that portion of the Bay is not as severe as is predicted by current USEPA criteria or by existing Basin Plan objectives. USEPA criteria experts have reviewed the work by the City of San Jose and have corroborated the City's findings. San Jose's work was part of a larger effort to assess impairment in the Lower South San Francisco Bay, focusing on the overall health of the ecosystem and the use of "suites" of environmental indicators. The stakeholder process used concluded that impairment is unlikely in the South Bay for copper and nickel based on ambient dissolved metals concentrations and recommended a range of copper and nickel site-specific objectives (SSOs) for the Lower South Bay. As a result of these findings, Regional Board and USEPA Region IX staff support removing copper and from the 2002 303(d) list for the Lower South San Francisco Bay.

Based on prior work in the remainder of the Bay on copper and nickel toxicity, consideration has turned to the question of impairment of the rest of the Bay for copper and nickel. Additional studies are required to address this question.

An ongoing issue in the Lower South Bay is the degree to which phytoplankton toxicity should be considered in a listing decision. Some species of phytoplankton are very sensitive to low concentrations of free ionic copper. The

discussion to date on this topic has focused on: (a) whether the sensitive phytoplankton species are important to the San Francisco Bay ecosystem, (b) whether the sensitive species are present in the Bay; and (c) the fact that USEPA criteria development is not driven by the consideration of phytoplankton toxicity. These issues may also be relevant to the consideration of copper and nickel impairment in San Francisco Bay north of the Dumbarton Bridge.

PURPOSE

The purpose of this work plan is to describe studies that can be used to provide an understanding of the toxicity of copper and nickel in San Francisco Bay. It is further envisioned that the data collected will be adequate for use in a 303(d) listing decision and the development of potential site specific objective for copper and nickel. Finally, it is anticipated that the results from this study will provide information which will serve as a foundation for the establishment of translators for copper and nickel.

It is intended that this work plan will be reviewed and approved by interested parties as the basis for performance of initial field studies. The work plan will be used to establish budget estimates and to seek commitments from various parties to participate in the proposed studies. After completion of initial field work, the work plan will be reviewed and modified by experts serving on a technical review committee.

OBJECTIVES

The objective of this work is to evaluate impairment due to copper and nickel in the San Francisco Bay from north of the Dumbarton Bridge to the San Joaquin and Sacramento River Deltas. This impairment assessment will be a coordinated effort that will provide information useful to the State in preparing the 2002 303(d) list for San Francisco Bay. By coordinating the effort among various parties, the study will be more economical and will result in quality data that is collected and analyzed consistently. The work will also be a first step towards developing site-specific objectives for copper and nickel.

BACKGROUND

Prior Studies in San Francisco Bay

A number of prior studies have been performed in San Francisco Bay to address the aquatic toxicity of copper and nickel. These studies include the following:

- NPDES permit studies performed for the Cities of San Jose and Sunnyvale in Lower South Bay (Larry Walker Associates/Kinnetic Laboratories/CH2M Hill, 1990-1991)

- Copper and nickel speciation studies in Lower South Bay performed by UC Santa Cruz (Bruland et al, 1992)
- Site specific objectives studies performed throughout San Francisco Bay for the Regional Water Quality Control Board (SR Hansen and Associates, 1991-1992)
- Nickel Toxicity tests in South San Francisco Bay (Institute of Marine Sciences for City of San Jose 1998)
- Site specific objectives studies performed in Lower South Bay by the City of San Jose (1996 - 1997)
- Nickel speciation work conducted by David Sedlak (UC Berkeley) (Sedlak, Phinney, and Bedsworth 1997, and Sedlak, Bedsworth and Jenkins 1998)

Key Findings of Prior Studies

These studies have been evaluated and summarized in the Impairment Assessment Report for South Bay prepared for the City of San Jose (Tetra Tech, August, 1999). The following key findings from these studies were identified in that report (page 4-43):

- The toxicity of copper and nickel is less in ambient site-water than the national water quality criteria predict (e.g. Water Effect Ratio¹ (WER) values are significantly greater than 1.0);
- The amount of bioavailable copper and nickel is reduced by the presence of components which make up the apparent complexing capacity of Lower South San Francisco Bay. These components can bind with copper and nickel, making them biologically unavailable (e.g. natural or anthropogenic organic ligands) or may compete for receptor sites on, or in, the organism (e.g. manganese and iron);
- The apparent complexing capacity is greatest in the extreme northern and southern portions of San Francisco Bay;
- The amount of bioavailable copper decreases from North to South in the Lower South Bay;
- The national criteria for copper and nickel are over-protective of the beneficial uses of Lower San Francisco Bay; and

¹ A WER is the ratio of toxicity of a given pollutant in laboratory water to toxicity in site water. If the value of the water effect ratio exceeds 1.0, the site water reduces the toxic effects of the pollutant being tested.

- The Lower South Bay results could justify multiple WER values (i.e. one for the northern end, one for the southern most reaches).

These past studies have shown that WER values for copper typically exceed 1.0 in San Francisco Bay. This implies that the toxicity of copper to sensitive organisms is reduced by the water quality characteristics of the Bay and is less than predicted by USEPA criteria. Additional WER studies will provide information that could be used in assessing impairment, making a listing decision, and developing a site-specific objective for copper in the remainder of the Bay, north of the Dumbarton Bridge.

Because a national aquatic life criterion might be more or less protective than intended for the aquatic life in most bodies of water, EPA has provided guidance concerning three procedures that may be used to derive a site-specific criterion (USEPA 1994):

1. **The Recalculation Procedure** is intended to take into account relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site.
2. **The Indicator Species Procedure** provides for the use of a WER that is intended to take into account relevant differences between the toxicity of the metal in laboratory dilution water and in site water.
3. **The Resident Species Procedure** is intended to take into account both differences in sensitivities of aquatic organisms and differences in toxicity of site water and lab water.

The Indicator Species procedure is based on the assumption that characteristics of ambient water may influence the bioavailability and toxicity of a pollutant. Acute toxicity in site water and laboratory water is determined in side by side toxicity tests using either resident species or acceptable sensitive non-resident species which are used as surrogates for the resident species. The difference in toxicity values, expressed as a WER, is used to convert a national concentration criterion for a pollutant to a site-specific concentration criterion.

For copper, the City of San Jose used the Indicator Species Procedure in its Impairment Assessment. Observed WER values ranged from 2.7 to 3.5 based on measured dissolved copper. The recommended range of chronic SSOs for the lower South Bay resulting from the Impairment Assessment was 5 to 12 ug/l dissolved copper. EPA reviewed this work and found that the species used were appropriate, the data valid and the conclusions reasonable (USEPA July 27, 1998).

For nickel, a combination of the Indicator Species and Recalculation procedures was used to develop site-specific modifications to the national water quality criterion. The recalculation of the national chronic criterion for dissolved nickel resulted in a range from 12 to 24 ug/l. EPA reviewed this work and found that the species and methodologies that were used were appropriate for developing site specific modifications to the nation water quality criterion for nickel. As a result, the finding derived in Lower South Bay is applicable to the rest of the Bay. As such, no additional toxicity testing is required to set appropriate nickel objectives for other regions of the Bay.

AMBIENT DATA FOR SAN FRANCISCO BAY

The Regional Monitoring Program for Trace Substances in the San Francisco Estuary collects copper and nickel data and additional water quality data at various locations in the Bay. The RMP monitoring sites are located predominately in the deep channel ("spine") of the Bay.

RMP sampling started officially in 1993 (pilot work began in 1989) and continues to present. Until 2000, water column samples were taken three times per year (one in the wet season, one in the declining Delta outflow hydrograph in the spring, one in the dry season). Effective in 2000, water column samples are taken twice per year (wet and dry seasons). Sediment samples are also taken twice per year.

The RMP data that are routinely collected include the following:

Table 1 RMP Sampling Constituents

Water Column		Sediment	
Conventional WQ Parameters	Trace elements (dissolved and near total)	General Characteristics	Trace elements
conductivity		%clay	arsenic
DOC (dissolved organic carbon)	arsenic	%silt	cadmium
DO (dissolved oxygen)	cadmium	%sand	chromium
hardness	chromium	%gravel+shell	cobalt
pH	cobalt	depth	copper
phaeophytin (a chlorophyll degradation product)	copper	ammonia	iron
salinity	iron	Hydrogen sulfide	lead
temperature	lead	pH	manganese
total Chlorophyll-a	manganese	TOC (total organic carbon)	mercury
TSS (total suspended solids)	mercury	total sulfide	nickel
Dissolved phosphates	nickel		selenium
dissolved silicates	selenium		silver
dissolved nitrate	silver		zinc
dissolved nitrite	zinc		
dissolved ammonia			

For the purposes of this work plan, levels of dissolved copper and nickel in the water column are of particular interest. Data for these parameters for the period 1993 to 1998 taken at various RMP sampling sites are summarized in figures contained in Appendix A. These data are shown in comparison to the CTR's chronic saltwater criteria for copper (3.1 ug/l) and nickel (8.2 ug/l). Note that the Lower South Bay effort resulted in a recommended SSO range for copper between 5 and 12 ug/l and for nickel between 12 and 24 ug/l.

MODELING RESULTS

Hydrodynamic modeling² of dissolved copper concentrations in San Francisco Bay has been performed by RMA Inc. for several of the Bay Area Dischargers Association (BADA) agencies. Results of the modeling, including dissolved copper concentration contours for various stages of the tidal cycle, were used in to assist in the selection of monitoring locations. Several figures showing model results are included in Appendix B. These figures illustrate the model's prediction of a dissolved copper gradient in San Pablo Bay and show expected concentrations in other parts of the Bay during ebb and flood tide.

LIMITATIONS OF EXISTING INFORMATION

The following data gaps currently restrict our understanding of copper and nickel toxicity in San Francisco Bay north of the Dumbarton Bridge:

- Water quality information (e.g. dissolved copper and nickel concentrations) in the shallow mudflat and slough areas
- Dissolved copper toxicity data for *Mytilus edulis*
- Copper speciation data in deep and shallow areas

The proposed work plan contains data collection activities intended to address these data limitations.

HYPOTHESES

Below are some hypotheses that have been identified for the development of this workplan. These hypotheses are interrelated and it is not necessarily the intent of this workplan to verify each of these singularly. The inherent variability in natural systems will require the study design and subsequent management decisions to be adaptive. The study elements were developed using these hypotheses as a starting point.

² 2-D Vertically averaged finite element analysis of San Francisco Bay performed by RMA, Inc.

- H1: The toxicity of copper is less in ambient site water north of the Dumbarton Bridge than the national water quality criteria predict (e.g. WER values are significantly greater than one)
- H2: The amount of bioavailable copper in San Francisco Bay north of the Dumbarton Bridge is reduced by the presence of components that bind with copper and/or compete for receptor sites on or in the organism.
- H3: Copper toxicity in ambient waters does not vary significantly between seasons, despite variations in copper concentrations.
- H4: While dissolved copper concentrations may increase along a gradient from deep to shallow waters in San Pablo Bay and Lower Bay, toxicity does not increase towards the shore due to greater organic complexation and binding capacity in shallow areas.
- H5: The national criteria for copper and nickel are over-protective of beneficial uses in San Francisco Bay north of the Dumbarton Bridge.
- H6: Copper speciation information can be used to evaluate phytoplankton toxicity.

PROPOSED APPROACH

Proposed Elements of Study

Copper

The focus of the work plan is on the collection of data to improve our understanding of the aquatic toxicity of copper in San Francisco Bay north of the Dumbarton Bridge. Work is comprised of three main elements.

- **Toxicity Testing**
Toxicity tests will be used to develop water effects ratios (WERs). A WER is expected to appropriately take into account the (a) the site-specific toxicity of metal and (b) synergism, antagonism, and additivity with other constituents of the site water (USEPA 1994). If the value of the water effect ratio exceeds 1.0, the site water reduces the toxic effects of the pollutant being tested. Adjustment to the acute and chronic EPA criteria are made by multiplying the EPA's ambient water quality criteria values (e.g., 3.1 ug/L dissolved copper) by the water effects ratio.

Toxicity tests in support of the development of WERs will be conducted for selected sites in the Bay during two different seasons. Detailed methodology of the testing is provided below. The methodology is based on procedures employed in the City of San Jose's Site Specific Objective study, including

the use of the indicator organism *Mytilus edulis* and adherence to EPA protocols. The toxicity study has been designed to test hypotheses regarding copper toxicity in the Bay, to aid in assessing impairment, to provide information useful in making a 303(d) listing decision, and to support the development of a site-specific objective. Preliminary sites have been selected based on the Bay's hydrodynamics, existing RMP sampling sites, and the need for investigation into the shallow areas of the Bay. It is intended that the first sampling run will be spatially diverse in order to provide data to a technical review committee who can then make recommendations for modifying the study.

- **Water Quality Analysis**
Analysis for conventional water quality parameters and some trace metals will be conducted for each site in the study. This information is intended to augment existing RMP data, to provide data required for the development of translators, and to aid in the interpretation of toxicity test results.

In addition, some constituents not presently included in RMP monitoring will be included in this study to provide information useful to the national effort to develop a Biotic Ligand Model (BLM). The BLM was created to evaluate bioavailability and toxicity of metals that have been discharged into surface water. The model takes into consideration several water quality parameters, including hardness, dissolved organic carbon, chloride, pH, and alkalinity. USEPA is currently considering the BLM as an alternative to WER studies in the development of site specific criteria. The Water Environment Research Foundation (WERF) is working closely with EPA in the development of this model. At this stage, the model has been developed and is being calibrated and beta-tested for copper and silver. Water quality constituents required as inputs into the model will be collected as part of this study in the hopes of providing useful data to BLM researchers and to ensure the data set collected could be used in the BLM at a later date. The specific constituents to be added to this workplan to support the BLM are: magnesium, calcium, and alkalinity. The costs for obtaining this data will be minor.

- **Copper Speciation**
One of the areas of uncertainty identified in the South Bay's Impairment Assessment Report was metal speciation and the processes that influence it. Not all copper present in San Francisco Bay waters is bioavailable. Trace metals, such as copper and nickel, can exist in a variety of chemical forms (species) that influence their toxicity to aquatic organisms. Free ionic copper is the primary toxic form of copper, while copper that is complexed with strong organic ligands is not similarly bioavailable for uptake by aquatic organisms (Donat, Lao, and Bruland 1994, Moffet et. al 1997, Impairment Assessment Report, 1999).

Previous studies in South San Francisco Bay have found that adsorbed forms and organic complexes make up a major portion of the total copper in the South Bay water column. Whether this holds true for the remainder of the Bay has not yet been explored.

Some copper speciation work has been identified for the proposed work plan for the following reasons: (a) it may address the mechanisms behind copper toxicity to sensitive species and allows for a more definitive explanation of WER effects in the Bay and (b) it may provide information which helps to address concerns regarding phytoplankton toxicity (the ratio of free ionic copper to free ionic manganese is a good predictor of phytoplankton toxicity.)

To ensure that uncertainties and technical issues are adequately addressed in the design of the speciation work, a small technical group will be assembled to discuss and design a speciation study that will complement the toxicity testing component of the work plan. Prospective participants in the study design include Ken Bruland (UCSC) and David Sedlak (UCBerkeley).

Nickel

The suggested work on nickel is limited to the collection of total and dissolved nickel concentration data in shallow water areas of the Bay. This information will supplement existing RMP data taken at deep channel sites, will be used to assess the potential for nickel toxicity using the recalculated nickel chronic criterion produced by the City of San Jose, and will be used to support the development of nickel translators.

GENERAL DESCRIPTION OF WORK

Sampling Plan

USEPA protocols favor the development of a robust data set (with an adequate number of samples). The sampling plan as proposed will result in a data set comparable in total number of samples to the City of San Jose's. The City of San Jose's work emphasized temporal variation (one WER event every two weeks for a year, at 3 sites). This resulted in 25 WER events for 3 sites. Of those, 5 had to be rejected for various reasons. This Impairment Assessment proposal shifts the emphasis toward spatial coverage. Sampling will include some deepwater and shallow water sites. The goal is four successful WER events, two summer and two winter at a variety of sampling locations (EPA protocol requires a minimum of 3 WER events).

Sampling Locations

The proposed sampling plan is to perform WER testing and water quality analysis on samples taken at a suite of shallow and deep water sites. Sites were selected with the intent of providing spatial coverage and representing different hydrodynamic segments of the Bay.

The following sites are proposed for the first sampling event:

Table 2 Sampling Stations and Locations
Deepwater Stations

RMP Station No	Station Name	Latitude (deg-min-sec)	Longitude (deg-min-sec)
BF20	Grizzly Bay	38-06-58	122-02-19
BF10	Pacheco Creek	38-03-05	122-05-48
BD20	San Pablo Bay	38-02-55	122-25-11
BD15	Western San Pablo Bay	38-06-66	122-29-00
BC10	Yerba Buena Island	37-49-40	122-20-40
BB30	Oyster Point	37-40-12	122-19-45
BB15	San Bruno	37-37-00	122-17-00
BA40	Redwood Creek	37-33-40	122-12-34

Shallow Water Stations

Station Name	Latitude	Longitude
Between BD20 and BD15 in San Pablo Bay	38-04-40	122-25-40
Eastern San Pablo Bay (mid-point transect)	38-05-05	122-21-30
Eastern San Pablo Bay (near shore transect point)	38-06-15	122-20-40
Lower Central Bay (mid-point on Lower Bay transect)	37-38-15	122-12-55
Lower Central Bay (near shore transect point)	37-38-50	122-11-05

The first four deepwater sites are in the North Bay. Grizzly Bay was selected as the first sample site because it is the close to the delta but has estuarine conditions. Delta sites will not be used because they are predominantly freshwater and would more appropriately be tested with a freshwater toxicity test. The Grizzly Bay and Pacheco Creek sites were both selected because they represent hydrodynamically different areas of the North Bay. The two sites in San Pablo Bay were selected because RMP data shows sporadic exceedances of dissolved copper criteria near the mouth of the Petaluma River and hydrodynamic modeling predicts an increasing dissolved copper gradient towards the shallows in the Bay.

The remaining four deepwater sites are in the Central and Lower Bay. Yerba Buena Island is located near the Bay Bridge. Oyster Point, San Bruno, and Redwood Creek, provide even spatial coverage of the remainder of the Central Bay. The City of San Jose conducted sampling to produce 8 WER observations at the San Mateo Bridge. The Redwood Creek RMP monitoring station is south of

the San Mateo bridge and has been included to provide confirmation of the City of San Jose's San Mateo WERs.

In addition to the deepwater stations above, the following shallow water sites are proposed:

Central Bay

Two sites between the Eastern shore and San Bruno site (BB15) to create a transect

San Pablo Bay

One site between the San Pablo Bay (BD20) and Petaluma River (BD15) sites to create transect

Two sites between Northeast shoal and San Pablo Bay (BD20) site to create a transect

The transects are intended to provide information regarding conditions in the shallow areas of San Pablo Bay. In San Pablo Bay, there is a known dissolved copper concentration gradient between the San Pablo Bay RMP station (BD20) and the Western San Pablo Bay RMP station (BD15). Sampling transects may help to determine whether this concentration gradient is unique to the Petaluma River, or is a typical near shore phenomenon. Hydrodynamic modeling suggests that it is a near shore phenomenon and that a copper concentration gradient exists throughout San Pablo Bay from the deep channel to the mudflats. The sampling information along the transects can be used to test this.

The transect in the Central Bay will provide information about copper toxicity in shoal areas. It is anticipated that copper concentrations may be higher near the shoals due to increased suspended solids. It is also anticipated that increased suspended solids may cause increased binding capacity that will lead to higher WERs near the shoals.

It is intended that the sites described above will be sampled in the first run to provide information to a technical review committee who can then make recommendations for study changes. The sites should provide a good spatial snapshot of WERs in the Bay in the dry season. After reviewing the data, some sites may not be included in subsequent testing. For example, if the Redwood Creek site is consistent with the City of San Jose's WERs for the San Mateo bridge, that site may be dropped from further sampling and the City of San Jose's San Mateo results will be used for that portion of the Bay.

Thus the number of proposed sites for the first sample run is 13. A map of proposed sampling sites is provided in Figure 1.

Sampling Period

A one year sampling period is proposed, beginning in summer 2000 and ending in summer 2001. The intent is to have sampling results available in the fall of 2001 for use in the 2002 303(d) listing process. EPA guidance states that the selection of the number and timing of sampling events should take into account seasonal considerations and should result in at least 3 WERs determined with the primary test species (in this case, *Mytilus edulis*) (USEPA 1994). The sampling period, as proposed, encompasses two dry seasons and one wet season. The goal of the sampling and toxicity testing will be to produce 4 successful WER events (2 dry season and 2 wet season). Funds have been budgeted to account for the possibility of failed WER events (i.e. failed spawn, failed reference toxicant test, etc.) which may require a repeat test.

Methodology

Water Collection

Clean techniques (USEPA 1994; Appendix 1) should be used throughout all phases of the sampling and lab work, including equipment preparation, water collection, sample handling and storage, and testing. Site water will be collected in 5-gallon cubitainers. Containers should be acid-rinsed, with the exception of the scintillation vials used for the WER testing. The scintillation vials should be rinsed with ultra pure water rather than acid due to associated toxicity of acid residue to bivalve embryos. Site water should be collected at slack high tide to minimize TSS and DOC. When sampled, site water should be placed in ice chests, on ice, until it reaches the laboratory.

Upon arrival at the laboratory, water quality of the raw water should be measured. Measurements should include temperature, pH, total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), total and dissolved copper, total and dissolved nickel, dissolved manganese, alkalinity, hardness, and salinity. Samples should be stored at $4 \pm 2^\circ\text{C}$. Site water samples should be used in the toxicity tests within 24-36 hours of collection.

Site Water Preparation and Salinity Adjustment

In order to remove potential predators, such as copepods, site waters should be filtered through a 50 μm filter screen. All toxicity tests should be conducted at ambient salinity of the labwater (30-32 ppt; see below). Since site waters are likely to be below ambient labwater salinity, they will require "salting up." Site water samples shall be salted up to ambient labwater salinity by using EPA synthetic salts (ASTM 1989). The City of San Jose has tested several different salts including commercial salts and found EPA synthetic salts to be the most appropriate. Potential contamination of site water during this process should be assessed through the use of equipment and container blanks. Following an approximate 15 to 30 minute equilibration period, the salinity of the salted up site

water should be confirmed and the salinity-adjusted water should be used immediately to prepare the toxicity tests.

All toxicity tests will be conducted at the ambient salinity of the collected laboratory water (30-32ppt). Artificial salts will be added to site water to bring its salinity up to 32ppt for testing. A salt water control will be run to verify that the salt additions are not contributing to the toxicity of the site water.

Laboratory water

Laboratory water used for the reference toxicant tests should be .45 µm filtered natural seawater obtained from Granite Canyon Marine Pollution Studies Laboratory. (This is the same laboratory water used by the City of San Jose in their WER study. The quality of this water is very high; it has been used since 1984 by the California Marine Bioassay Project to develop sensitive methods for testing discharges into California marine waters.) Seawater should be collected from a continuously running seawater system one to two days prior to testing. Upon arrival at the laboratory, the seawater should be stored at 4±2°C. Basic water quality (temperature, pH, TOC, DOC, TSS, alkalinity, hardness, and salinity) and trace metals (total and dissolved copper, total and dissolved nickel, dissolved manganese) should be determined prior to storage. Basic water quality and trace metals (copper, nickel, manganese) should also be determined for the laboratory water used in each WER event.

Toxicity Testing Procedure

Laboratory water/reference toxicant test water and site waters should be spiked with seven different concentrations of copper using a 0.7 dilution ratio. One liter of water should be prepared in a volumetric flask for each test. The flask can be used serially, first for the control water, and then for each of the seven concentrations, in order of increasing concentration. From the flask, 10 ml should be taken for each scintillation test vial. There should be five replicate test vials for each of the seven concentrations, plus a set of controls. (total of 40 scintillation vials). The remaining water should be used for chemical analysis.

*Mytilus edulis*³ will be used for the toxicity tests. Animals will be obtained from the Carlsbad Aquafarm, Carlsbad, CA. and shipped overnight on ice for each WER event. Test vials should be inoculated with fertilized embryos at or beyond the 2-celled stage. Test vials should be capped and incubated for 48-hrs at 15±1°C. The test endpoint will be the proportion of normal D-shaped, straight-hinged larvae with completely developed shells in each test container relative to the number of normal embryos in the initial density vials. A minimum of ten

³ The City of San Jose reports that genetic electrophoretic analysis of the animals presumed to be *M. edulis* indicate this species is actually *M. galloprovincialis*. However, this is believed to be the same species used by Toxscan and SAIC and referred to as *M. edulis* in the national Saltwater Copper Addendum (EPA 1995). Therefore, the species name reported by EPA will be used to avoid confusion.

initial density vials are recommended. Larvae should be counted with the use of an inverted compound microscope. A reference toxicant test will be conducted with each WER event in order to determine whether the bivalve embryos are responding normally to toxicant stress. This test will also serve as the laboratory water test for use in the determination of WER values.

Chemical Analyses

Trace metals analysis should be performed using a chelation/extraction technique to remove positive salinity interferences. EPA guidance recommends that the detection limit be less than one-tenth of the CCC or CMC that is to be adjusted. Analytical measurements should be sufficiently sensitive and precise that variability in analyses will not greatly increase the variability of the WERs (EPA 1994)

Following each testing event, the chemistry results should be reviewed. Samples should be re-analyzed if measurements are outside reasonable limits (i.e. <80% ratio of nominal to total measurements, dissolved value is greater than total value, etc.)

The WER procedure recommends that initial and final copper measurement be made on all concentrations used in determining the endpoint. For this study, only initial total and dissolved copper measurements will be made for selected concentrations and the control. Subsequent statistical analyses and WER calculation will be based only on measured copper concentrations at the beginning of the test, rather than on a time-weighted average of initial and final values. This is a conservative approach, as using only initial values for dissolved copper is likely to produce a lower WER. One test will be run in which both initial and final values measured to verify that copper recovery in lab water tends to be lower than recovery in site water, yielding a higher WER if time-weighted averages are used in WER calculation rather than initial concentrations only.

Secondary Testing

At least one WER event will be performed with a secondary organism that is taxonomically different from the primary test organism, *Mytilus edulis*. The selection of the organism and the timing of the tests will be determined after the technical review committee has met and reviewed the results of the initial WER events.

QA/QC

The main goal of this work is to produce high quality data that can be used by regulatory and non-regulatory decision-makers with confidence. Several Quality Control/Quality Assurance measures will be built into the study to ensure the validity and reproducibility of the results. Clean techniques will be employed in

all aspects of the study. Chemistry measurements will include a method blank and a standard (certified reference material). Blind standards will be used in chemistry samples for each WER event.

Program Management

Administration

An entity will be needed to administer contracts and to collect and disperse funds. BADA has been proposed to provide these services.

Monitoring

A program coordinator will be needed to manage the performance of field and laboratory studies. The coordinator should be on board at the outset of the program and should continue throughout the data collection period.

Data Analysis

The data to be collected will be used to address main objectives of the study and to test the hypotheses which were identified earlier.

Data will be evaluated for compliance with quality control criteria at the end of each sampling event. Poor data must be rejected and replaced in a timely fashion. Close scrutiny will be required over the WER testing and copper speciation work.

Reporting

The results of the proposed studies will be summarized in a technical report. The report must describe the overall program and must clearly show the results from the toxicity testing and chemical analyses. It is important that the completed report be submitted to Regional Board staff in the fall of 2001 to allow adequate time for Regional Board staff to make determinations regarding the 2002 303(d) list due to EPA on April 1, 2002.

External Review

A technical review panel consisting of experts in the field of toxicity, ecology and chemistry shall be assembled to assist in the review of the work plan and subsequent deliverables. Suggested panel members include David Hansen (ex-USEPA criteria expert, Glen Thursby (USEPA), David Sedlack (UC Berkeley), Russ Flegal (UC Santa Cruz), Ken Bruland (UC Santa Cruz). A subset of this group will be enlisted to assist in the development of the copper speciation work element.

A process for review of the technical report by important state and federal agencies will be established.

Stakeholder Outreach

Efforts should be made to reach out to other interested parties to solicit input regarding all aspects of the proposed program. This may include holding a technical workshop to review methods, results and conclusions for the proposed studies. The budget for this work plan does not include an allocation for performance of outreach activities.

Regulatory Liaison

The program will need to actively involve RWQCB, USEPA, and DFG staff throughout the process. RWQCB staff will need to approve the workplan and any future changes. It will be requested that a member of RWQCB staff be assigned specifically to this impairment assessment to provide consistent support and input throughout the length of the study.

Program Manager

A program manager will be selected to oversee and coordinate all the above elements of the program.

Estimated Costs

A summary of estimated costs is shown in Table 3.

Table 3. Summary of Estimated Costs for Proposed WER Testing and Chemical Analysis*

WER Testing							
Station	Description	Summer, 2000 WER	Winter 2001 WER	Winter 2001 WER 2nd species ¹	Summer 2001 WER	Rerun ¹	Totals
Deep							
BF20	Grizzly Bay	4,600	4,600	9,200	4,600	4,600	
BF10	Pacheco Creek	4,600	4,600	9,200		4,600	
BD20	San Pablo Bay	4,600	4,600	9,200	4,600	4,600	
BD15	Western San Pablo Bay	4,600	4,600	9,200	4,600	4,600	
BC10	Yerba Buena Island	4,600	4,600	4,600	4,600		
BB30	Oyster Point	4,600	4,600	4,600			
BB15	San Bruno	4,600	4,600	4,600	4,600		
BA40	Redwood Creek	4,600					
Shallow							
	Transect: Central Bay	9,200	9,200	9,200	9,200		
	Transect: San Pablo Bay to Petaluma	4,600	4,600	4,600			
	Transect: San Pablo Bay to Northern Shoal	9,200	9,200	9,200			
TOTALS		59,800	55,200	73,600	32,200	18,400	239,200
Chemical Analysis							
Station	Description	Summer, 2000 Std Chem	Winter 2001 Std Chem	Winter 2001 Std Chem	Summer 2001	Rerun	
Deep							
BF20	Grizzly Bay	475	475	475	475	475	
BF10	Pacheco Creek	475	475	475		475	
BD20	San Pablo Bay	475	475	475	475	475	
BD15	Western San Pablo Bay	475	475	475	475	475	
BC10	Yerba Buena Island	475	475	475	475		
BB30	Oyster Point	475	475	475			
BB15	San Bruno	475	475	475	475		
BA40	Redwood Creek	475					
Shallow							
	Transect: Central Bay	950	950	950	950		
	Transect: San Pablo Bay to Petaluma	475	475	475			
	Transect: San Pablo Bay to Northern Shoal	950	950	950			
TOTALS		6,175	5,700	5,700	3,325	1,900	20,900
Copper Speciation							
TOTALS		0	40,000	0	0		40,000
Administration and Report Preparation							
TOTALS							100,000
Contingency							
TOTALS							50,000
Combined Total							450,100

* These are placeholder costs based on current workplan design. It is anticipated that the study design will be revised based on the results of the first sample run.

¹ May be necessary due to failed spawn or other factor that invalidates WER.

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Appendices

A - RMP Data Summaries

B - Modeling Results

Table 7 - Event 1 Data Summary

Site	Site Description	Date Collected	Temp (oC)	pH	D.O. (mg/L)	Salinity (ppt)	Ammonia (mg/L)	Hardness (mg/L as CaCO3)	Alkalinity (mg/L as CaCO3)	TSS (mg/L)	TOC (mg/L)	DOC (mg/L)	Total Cu (ug/L)	Diss. Cu (ug/L)	Total Ni (ug/L)	Diss. Ni (ug/L)	Diss. Mn (ug/L)	Diss. Cu EC50	Diss. Cu WER	Total Cu EC50	Total Cu WER
GC Seawater	lab water	9/3/00	11.3	8.02	9.8	33.2	< 0.1	4950	112	2.7	<1.5	<1.5	0.77	0.75	1.40	1.30	2.75	8.3 (N), 8.05 (C)		9.6 (N), 9.3 (C)	
BA40	Redwood Creek	9/7/00	4.9	8.13	8.2	29.0	< 0.1	4650	116	9.1	2.7	2.6	2.97	2.86	4.02	3.81	17.7	21.7	2.70	27.1	2.91
BB15	San Bruno	9/7/00	4.3	8.24	7.8	29.4	< 0.1	4550	104	8.3	2.0	<1.5	4.14	2.88	4.22	2.75	15.2	19.4	2.41	23.4	2.52
LCB01	L. Central Bay (Mid-point on Transect)	9/7/00	6.5	7.80	8.3	29.3	< 0.1	4610	115	6.3	2.9	2.0	3.07	2.45	3.96	3.62	15.1	20.1	2.50	23.1	2.48
LCB02	L. Central Bay (Near shore on Transect)	9/7/00	6.4	8.02	8.5	29.1	< 0.1	4490	118	5.4	4.7	4.6	3.41	2.76	4.44	3.85	13.7	19.4	2.41	23.2	2.49
BB30	Oyster Point	9/7/00	4.9	8.12	8.2	30.2	< 0.1	4850	108	6.0	2.3	<1.5	2.71	2.6	2.94	2.61	27.5	20.3	2.52	24.8	2.67
BC10	Yerba Buena Island	9/7/00	4.5	8.10	8.3	29.0	< 0.1	4580	106	6.7	1.6	<1.5	2.56	1.89	2.73	2.01	19.7	17.8	2.21	23.9	2.57
BD20	San Pablo Bay	9/5/00	8.2	7.92	9.2	23.9	< 0.1	3530	94	8.1	2.2	2.1	3.11	2.51	3.48	2.47	10.40	18.2	2.19	23.4	2.44
SPB01	SPB between BD15 & BD20	9/5/00	7.0	8.06	8.9	22.9	< 0.1	3400	94	17.6	2.2	1.5	4.28	2.52	5.03	2.56	12.2	16.7	2.01	24.7	2.57
BD15	Petaluma River (western SPB)	9/5/00	7.9	8.06	8.8	22.9	< 0.1	3500	99	59.2	4.5	3.0	9.09	4.17	14.09	4.87	54.9	22.4	2.70	35.9	3.74
SPB02	Eastern SPB mid-point on transect	9/5/00	7.4	8.37	9.5	23.7	< 0.1	3180	96	36.3	2.9	1.7	5.35	2.82	7.23	3.08	12.9	14.2	1.71	27.6	2.88
SPB03	Eastern SPB near shore on transect	9/5/00	7.7	8.10	8.6	27.6	< 0.1	3240	93	17.1	4.1	2.3	3.95	2.76	4.44	2.57	8.25	14.5	1.75	25.1	2.61
BF10	Pacheco Creek	9/5/00	15.2	7.84	9.1	7.9	< 0.1	1190	72	12.5	1.8	1.7	4.01	2.83	4.26	2.21	6.78	21.1	2.54	28.7	2.99
BF20	Grizzly Bay	9/5/00	16.2	7.96	8.8	5.3	< 0.1	824	66	13.9	2.0	2.0	4.09	2.76	4.31	2.15	8	14	1.69	21.9	2.28

(N) = for North Bay tests
(C) = for Central Bay tests

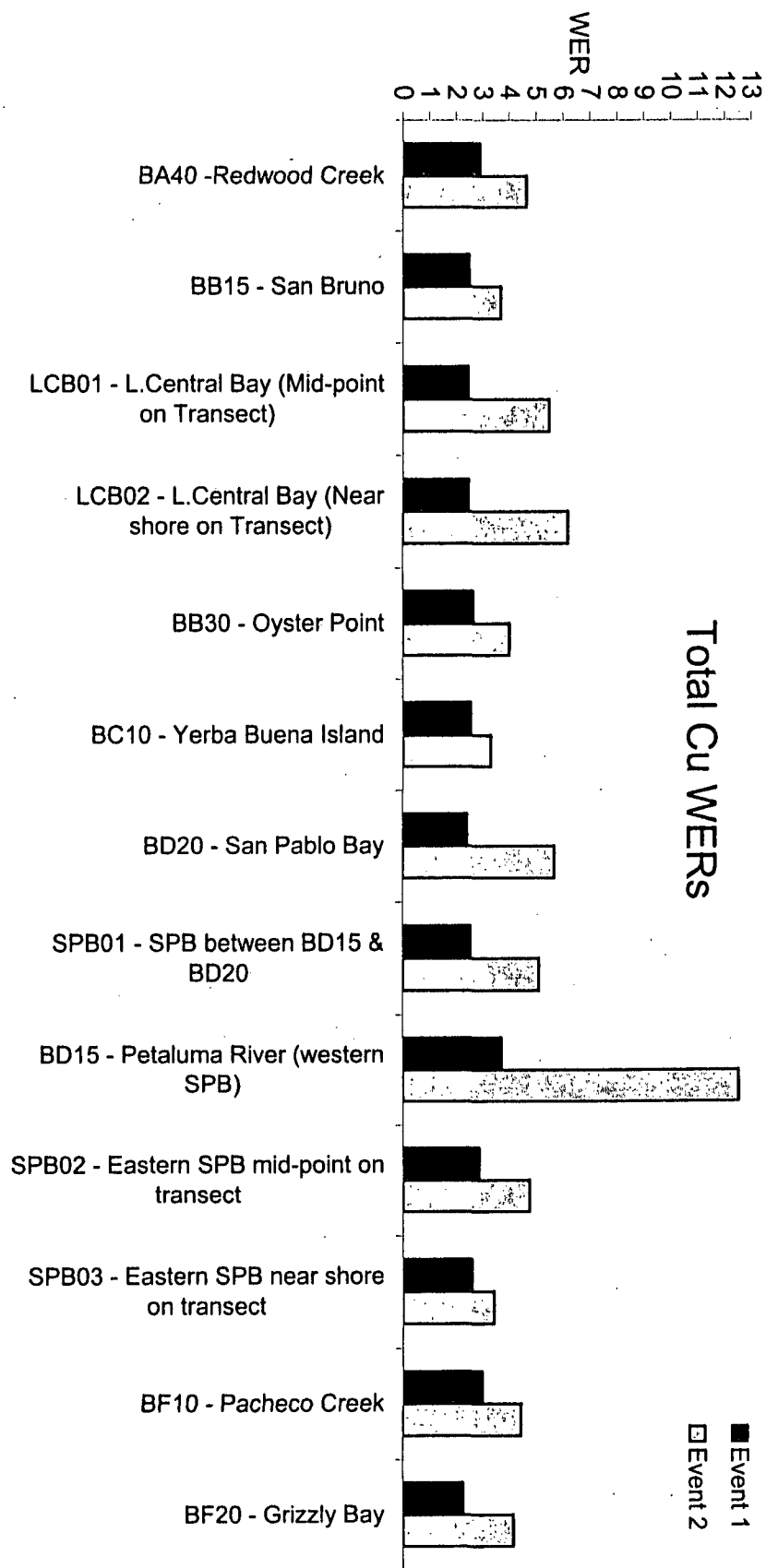
Table 8 - Event 2 Summary Table

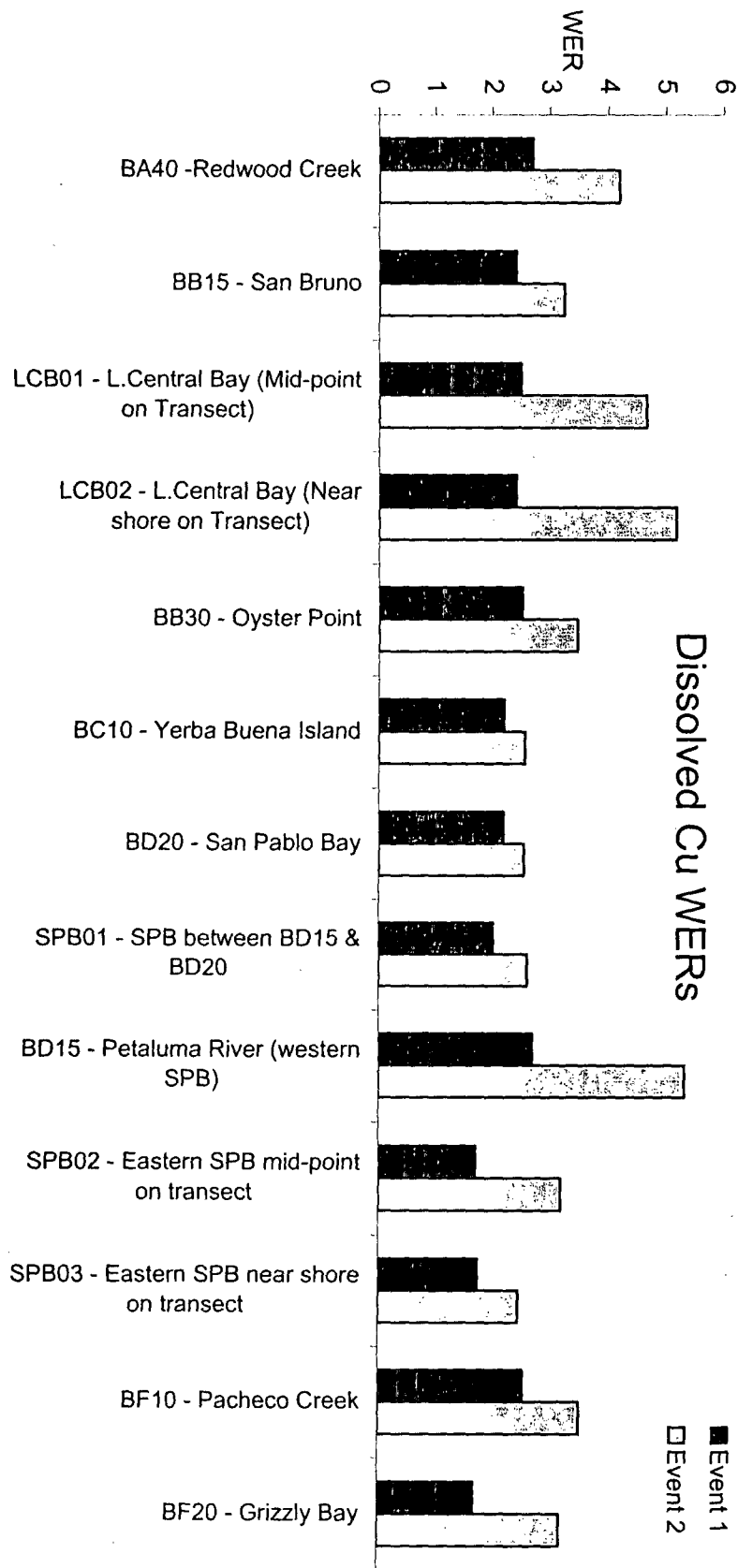
Site	Site Description	Date Collected	Temp (°C)	pH	DO (mg/L)	Salinity (ppt)	Alkalinity (mg/L as CaCO3)	TSS (mg/L)	TOC (mg/L)	DOC (mg/L)	SUVA	Total Cu (ug/L)	Diss. Cu (ug/L)	Total Ni (ug/L)	Diss. Ni (ug/L)	Diss. Mn (ug/L)	Diss. Cu EC50	Diss. Cu WER	Total Cu EC50	Total Cu WER
GC Seawater	lab water		measured in field				64	3	0.38	0.55	<1E-6, 0.0068	0.11	0.11	0.43	0.43	2.9	9.5 (N), 5.96 (C)		10.4 (N), 6.77 (C)	
BA40	Redwood Creek	2/15/01	9.7	8.05	11.5	26.4	90	22	3.3	3.2	0.0019	3.61	2.74	4.87	3.51	15	25.0	4.19	31.6	4.67
BB15	San Bruno	2/15/01	8.7	8.06	13.1	28.0	76	24	2.2	2.1	0.0024	2.78	2.07	4.35	3.20	8.3	19.3	3.24	25.1	3.71
LCB01	L Central Bay (Mid-point on Transsect)	2/15/01	9.2	8.05	13.6	26.5	98	33	3.6	3.2	0.0047	5.05	2.70	7.53	3.49	3.6	27.8	4.66	37.3	5.51
LCB02	L Central Bay (Near shore on Transsect)	2/15/01	9.7	8.09	11.0	25.1	95	30	3.6	3.3	0.003	4.10	3.02	5.87	3.75	8.1	30.9	5.18	42	6.20
BB30	Oyster Point	2/15/01	8.8	8.10	11.0	28.2	80	17.0	2.6	2.2	0.0018	2.77	2.15	4.20	3.03	2.7	20.7	3.47	27.3	4.03
BC10	Yerba Buena Island	2/15/01	9.0	7.97	10.7	29.1	71	21	2.8	1.7	<1E-6	2.17	1.26	3.81	2.16	5.6	15.3	2.57	22.5	3.32
BD20	San Pablo Bay	2/13/01	8.1	8.01	10.8	20.6	99	120	5.0	4.9	0.001	8.06	1.85	12.7	2.97	1.10	24.2	2.55	59.3	5.70
SPB01	SPB between BD15 & BD20	2/13/01	7.0	8.05	11.7	18.5	110	120	6.5	8.1	0.0011	7.53	2.42	10.8	3.22	0.77	24.8	2.61	53.4	5.13
BD15	Petaluma River (western SPB)	2/13/01	6.5	7.72	10.9	14.8	150	370	12.0	9.0	0.0033	21.6	4.31	47.6	17.2		50.5	5.32	130.5	12.55
SPB02	Eastern SPB mid-point on transect	2/13/01	7.3	8.05	11.1	19.0	120	68	5.2	4.8	0.0021	6.08	2.01	9.39	3.17	6.6	30.3	3.19	49.6	4.77
SPB03	Eastern SPB near shore on transect	2/13/01	7.6	8.01	11.1	19.4	100	48	4.8	4.5	0.0013	4.77	2.01	7.63	3.07	7.8	23.4	2.46	35.8	3.44
BF10	Pacheco Creek	2/13/01	7.6	7.89	12.1	6.0	170	46	9.7	9.6	0.0028	5.01	2.50	6.82	3.15	6.9	33.3	3.51	46.4	4.46
BF20	Grizzly Bay	2/13/01	8.4	7.88	12.1	6.3	170	66	9.4	10.0	0.0023	6.17	2.63	8.71	3.27	14	30.2	3.18	43.3	4.16

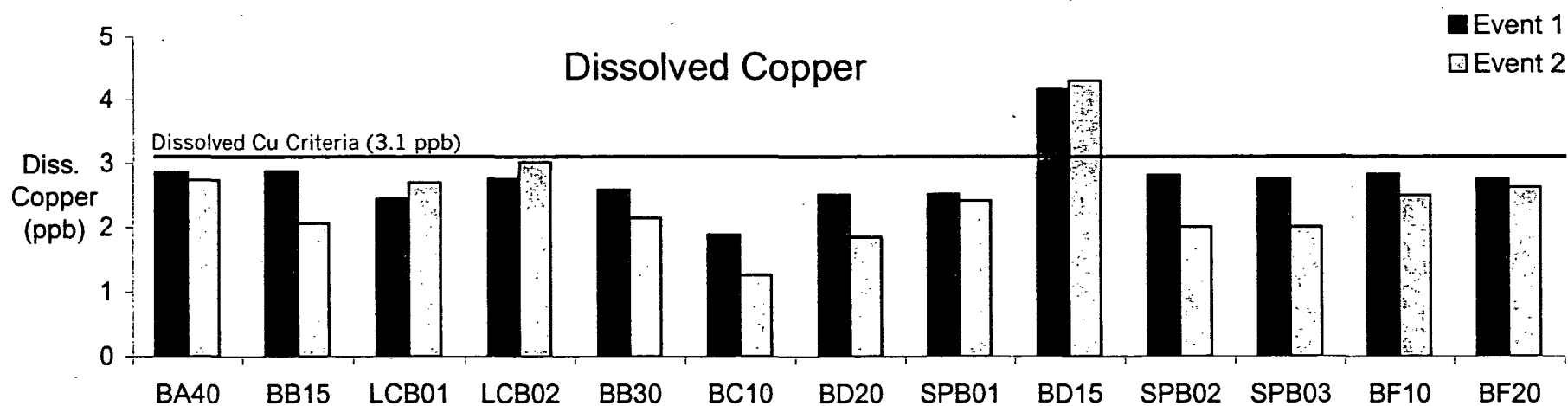
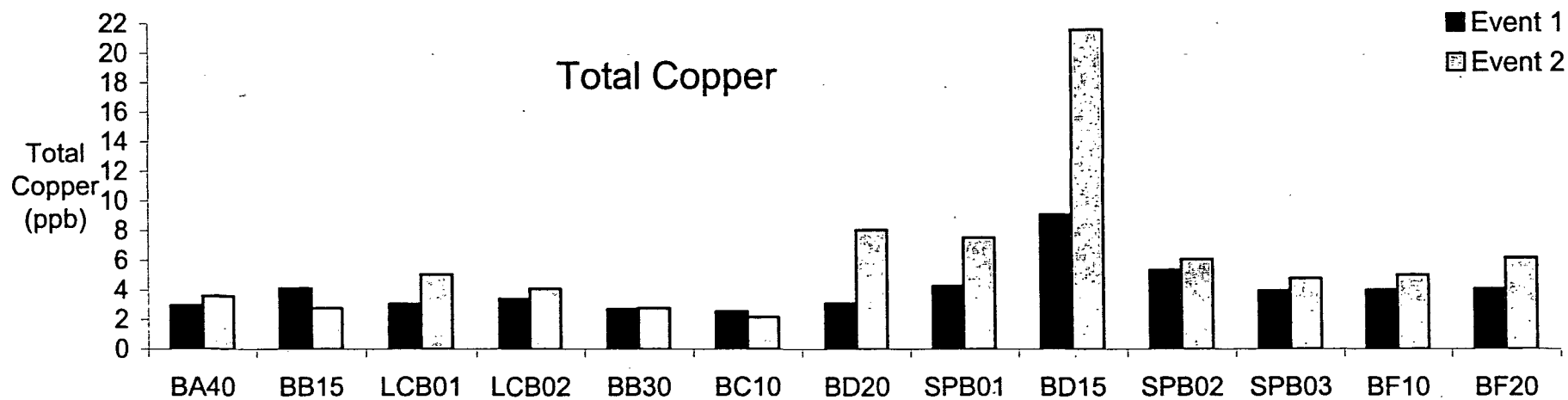
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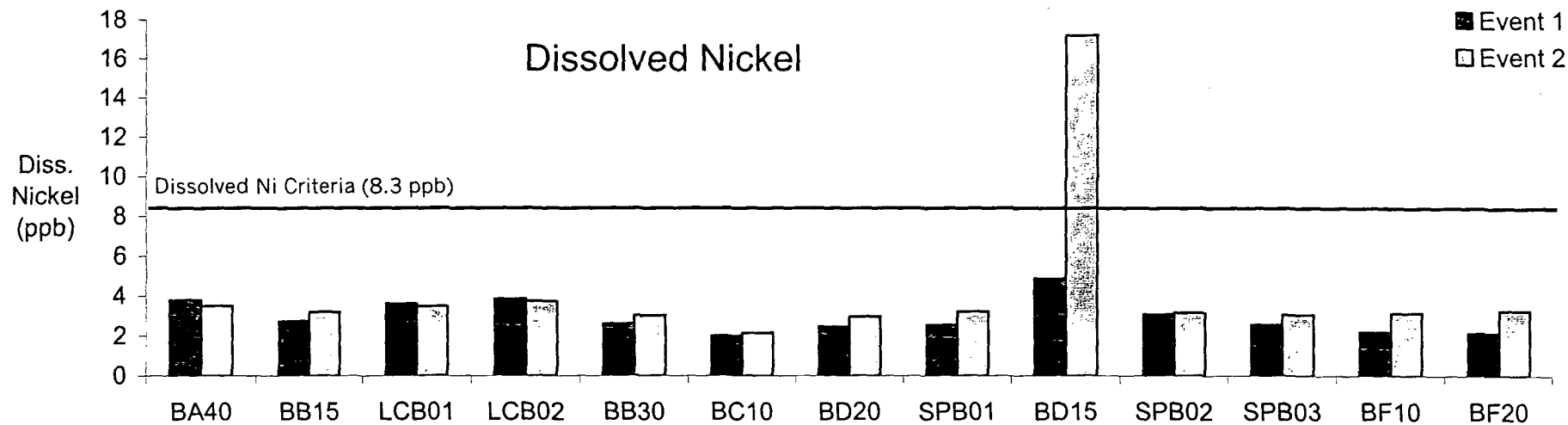
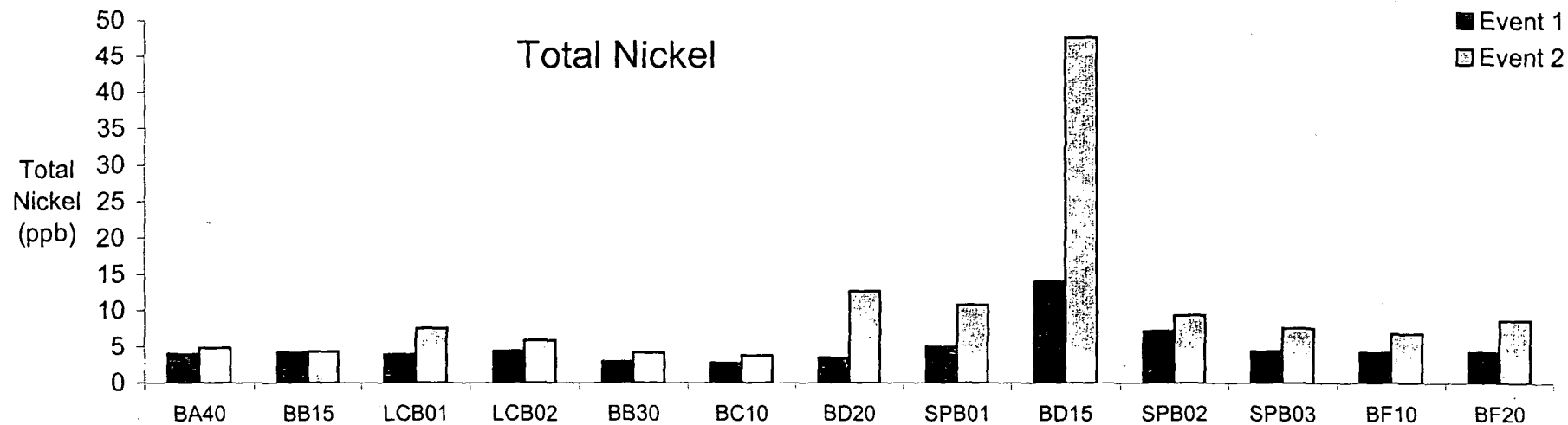
Table 9 - Biotic Ligand Model Summary

Site	pH	DOC (mg/L)	TOC (mg/L)	Alkalinity (mg/L)	DIC (mg/L)	Dissolved Mg (mg/L)	Dissolved Ca (mg/L)	Dissolved Na (mg/L)	Dissolved K (mg/L)	Dissolved Sulfate (mg/L)	Reactive Sulfide - Total (mg/kg)	Reactive Sulfide - Dissolved (mg/kg)	UVA
GC Seawater		0.55	0.38	64	13	1200	370	10000	250	2400	20	<2.5	<1E-6, 0.0068
BA40	8.05	3.2	3.3	90	<0.15	1300	400	10000	360	2600	15	<2.5	0.0019
BB15	8.06	2.1	2.2	76	<0.077	1200	380	10000	360	2500	15	<2.5	0.0024
LCB01	8.05	3.2	3.6	98	0.49	1300	390	10000	340	2600	20	<2.5	0.0047
LCB02	8.09	3.3	3.6	95	0.65	1300	400	10000	330	2300	25	<2.5	0.003
BB30	8.10	2.2	2.6	80	<0.077	1300	380	11000	350	2700	25	<2.5	0.0018
BC10	7.97	1.7	2.8	71	<0.077	1200	370	10000	350	2900	15	<2.5	<1E-6
BD20	8.01	4.9	5.0	99	<0.15	1500	430	9700	310	1900	15	<2.5	0.001
SPB01	8.05	8.1	6.5	110	<0.077	1400	430	9000	310	1800	20	<2.5	0.0011
BD15	7.72	9.0	12.0	150	0.16	1500	470	9400	290	2500	20	<2.5	0.0033
SPB02	8.05	4.8	5.2	120	<0.077	1400	430	9600	320	2000	15	<2.5	0.0021
SPB03	8.01	4.5	4.8	100	<0.077	1400	430	9700	320	2000	15	<2.5	0.0013
BF10	7.89	9.6	9.7	170	<0.077	1700	520	9100	290	2100	20	<2.5	0.0028
BF20	7.88	10.0	9.4	170	<0.077	1700	520	9300	280	2200	10	<2.5	0.0023

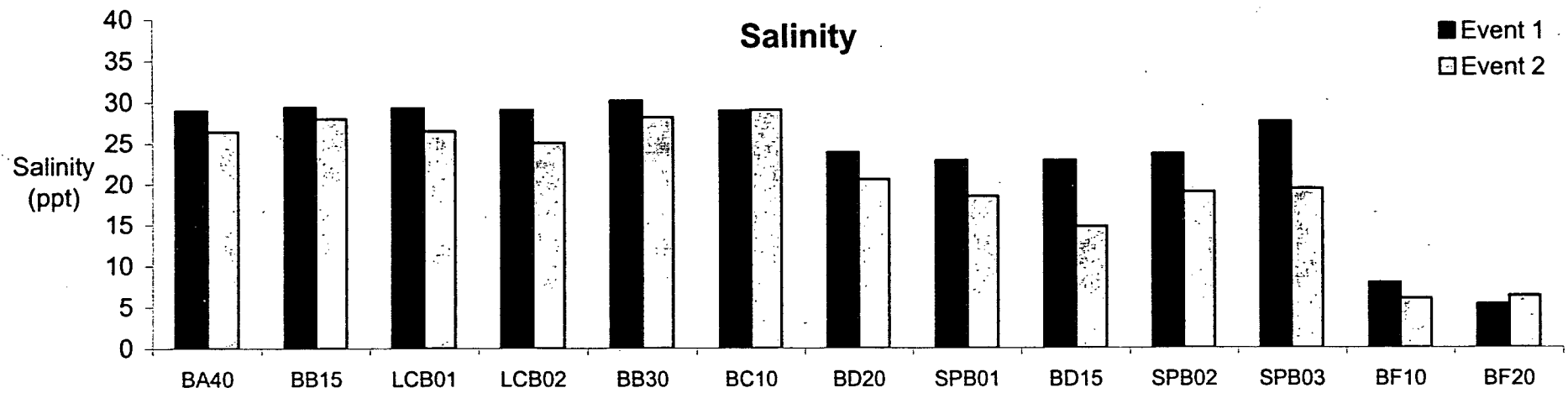


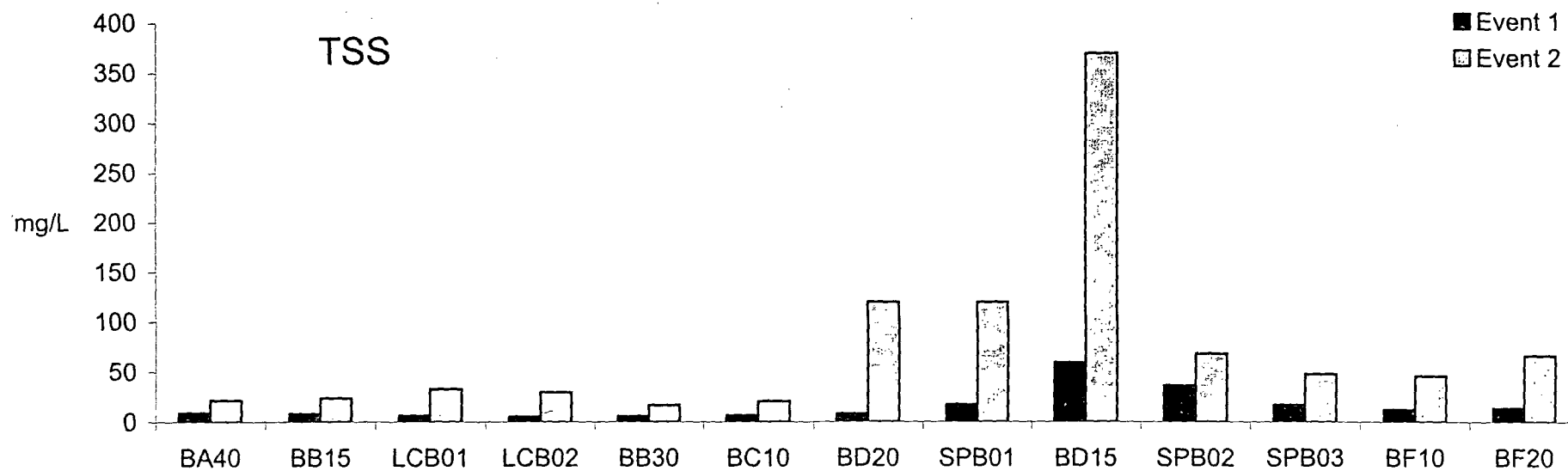


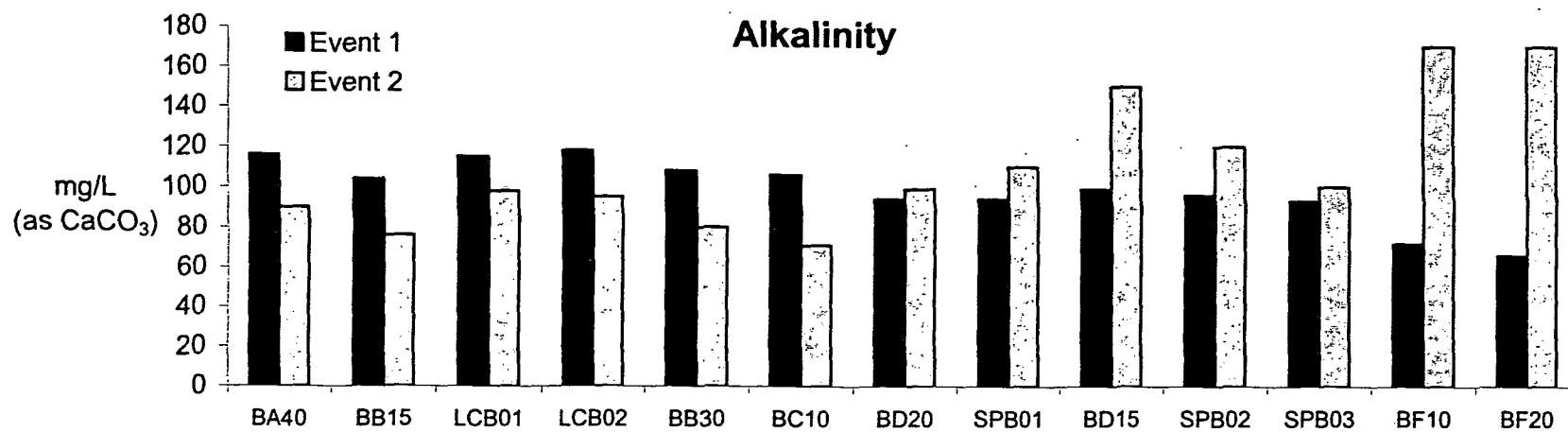


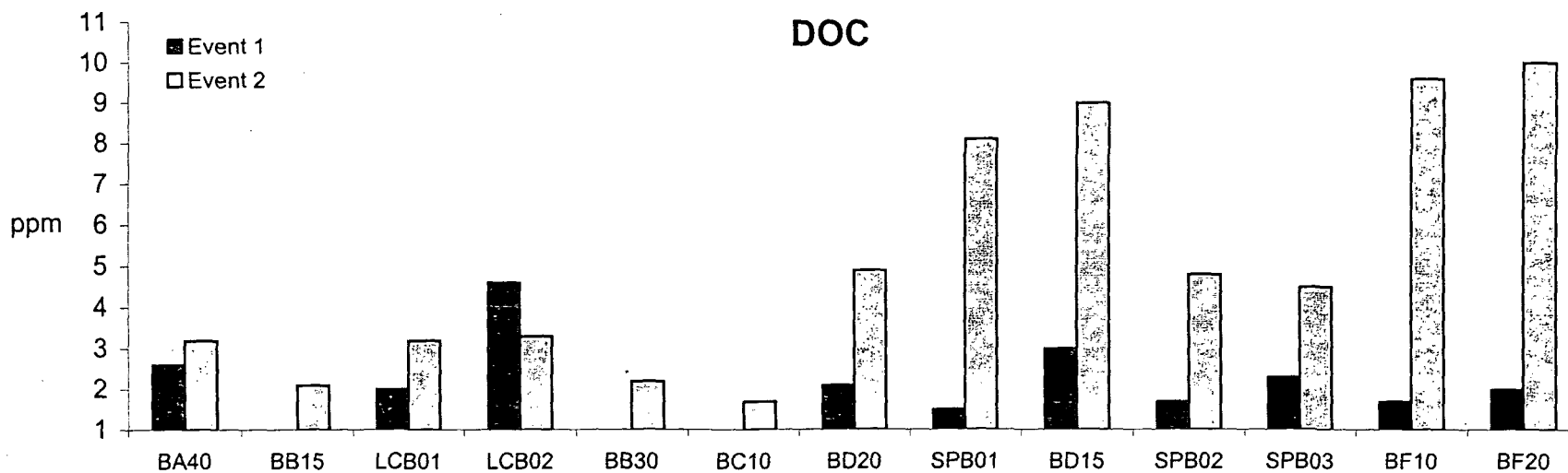
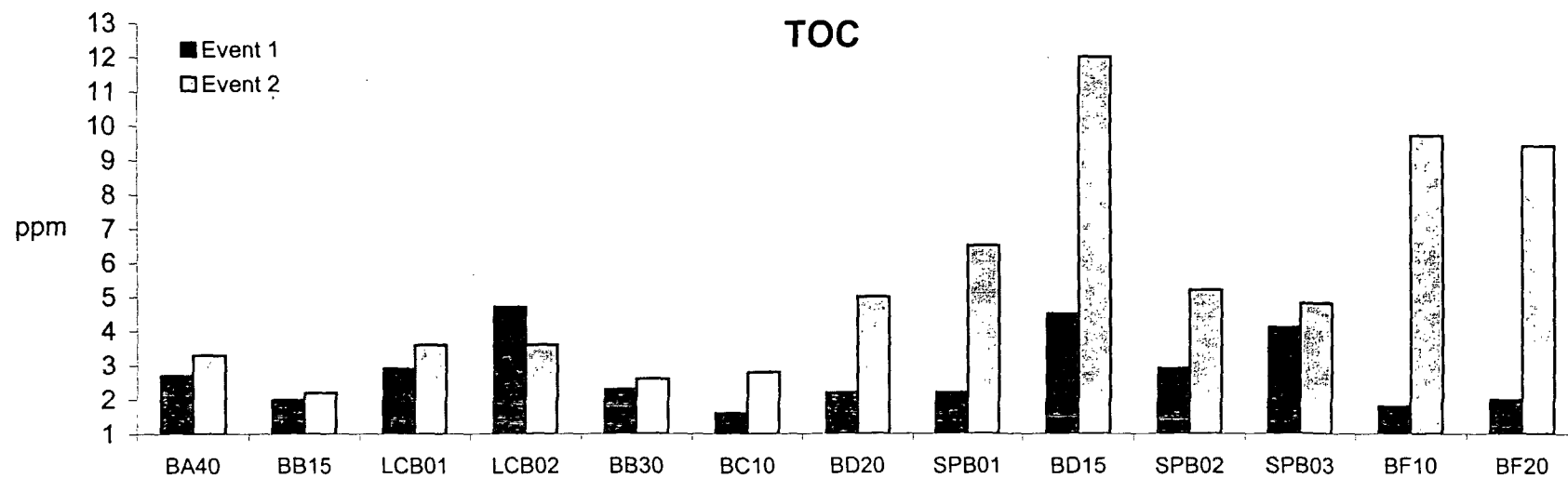


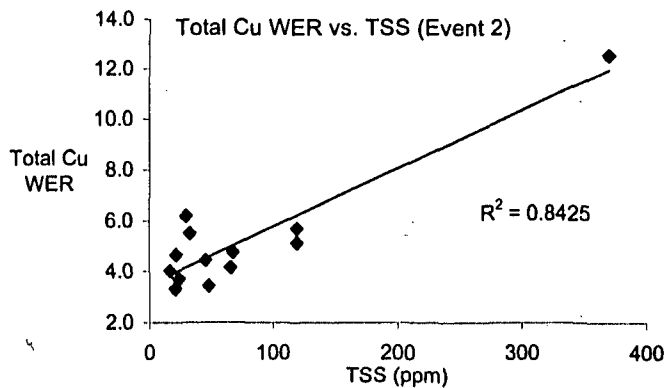
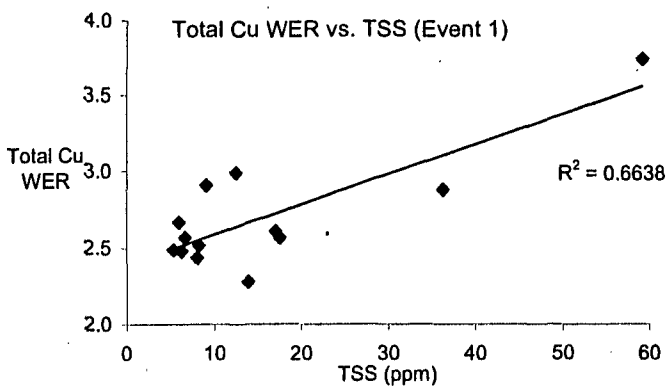
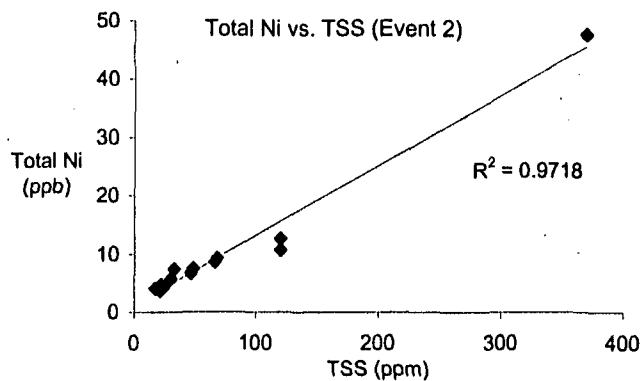
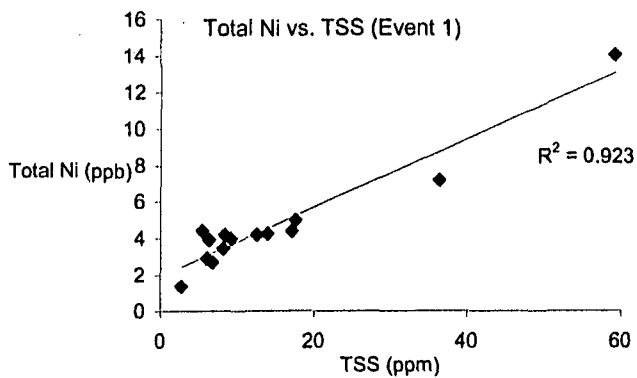
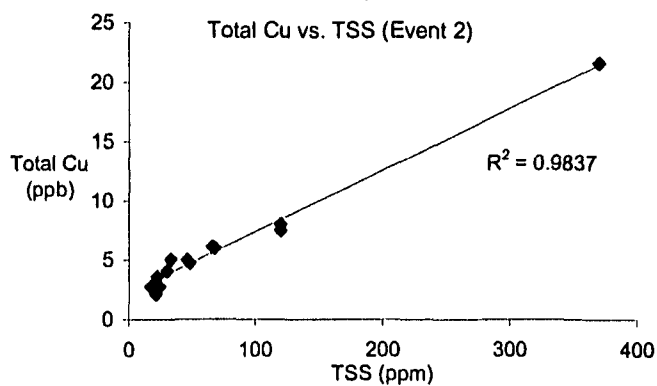
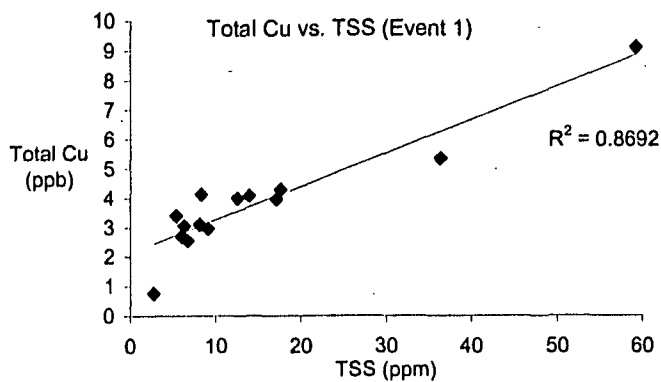
Salinity





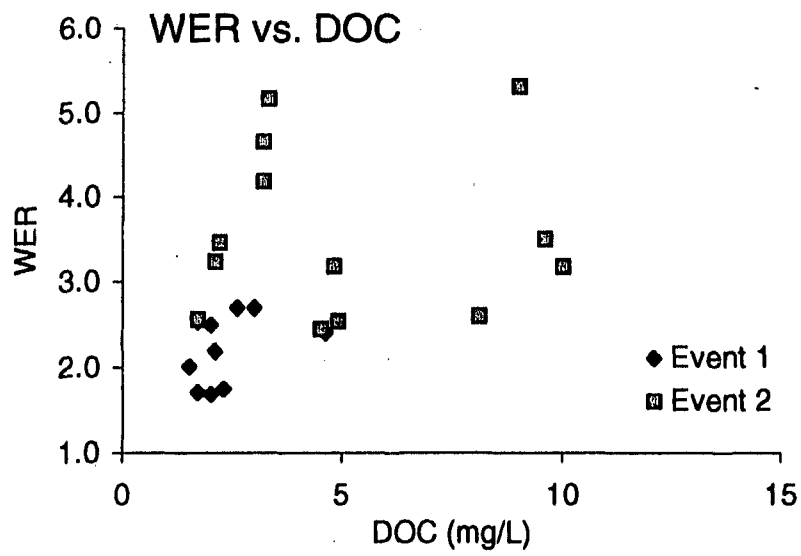
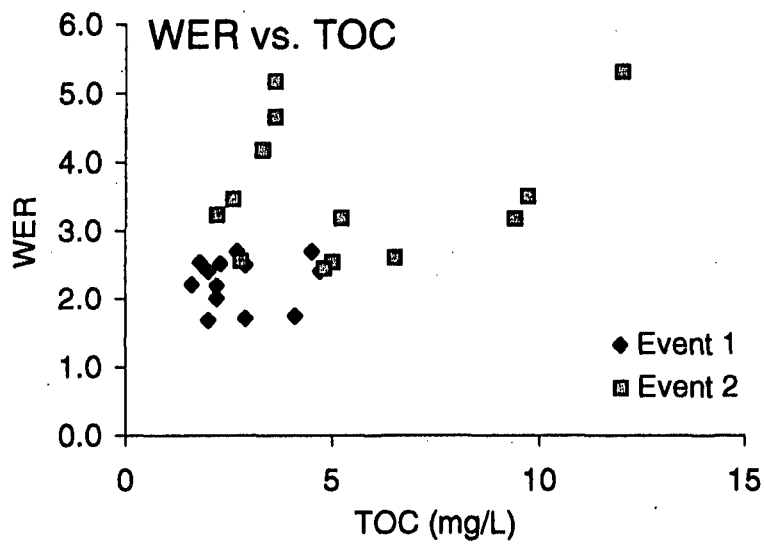


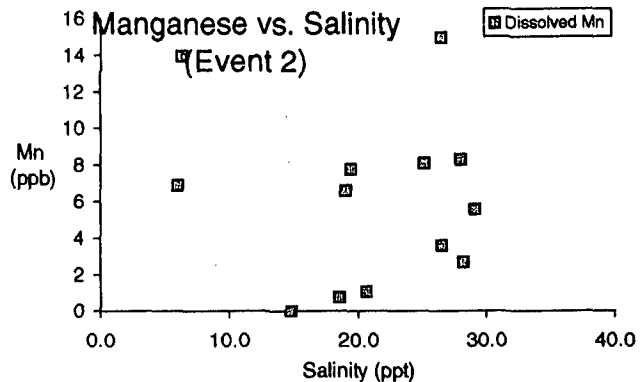
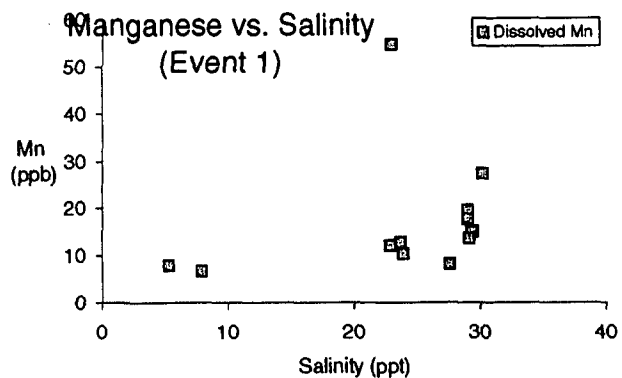
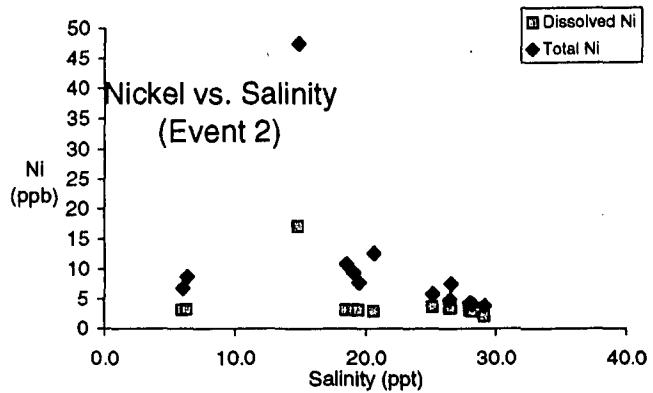
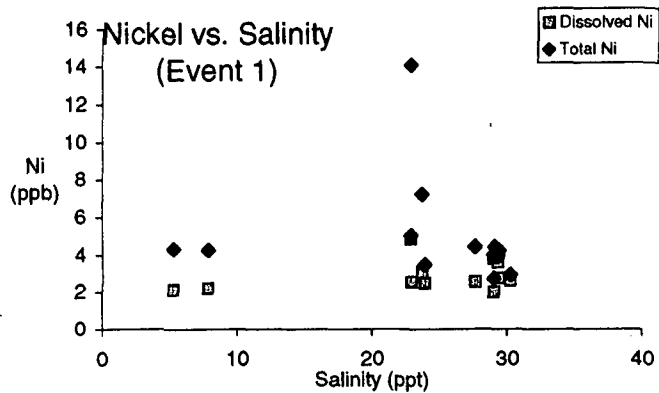
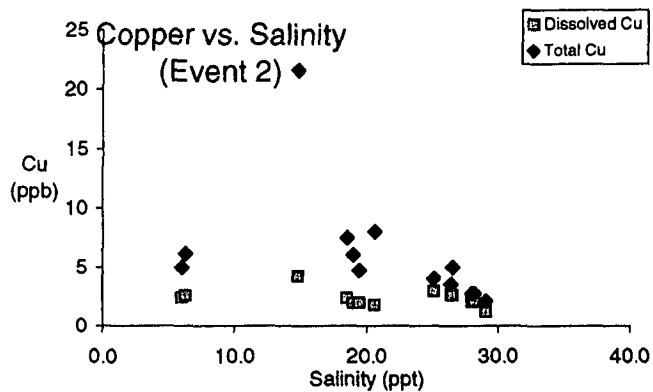
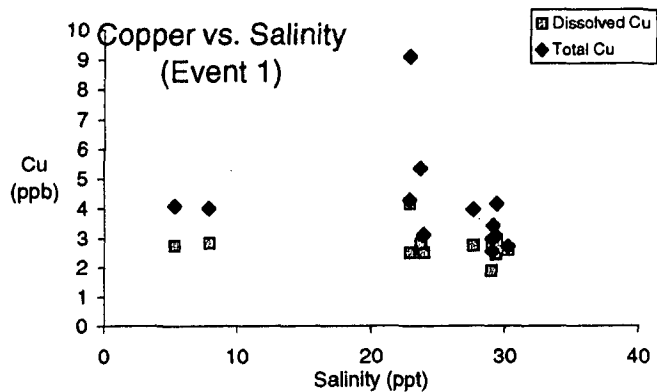


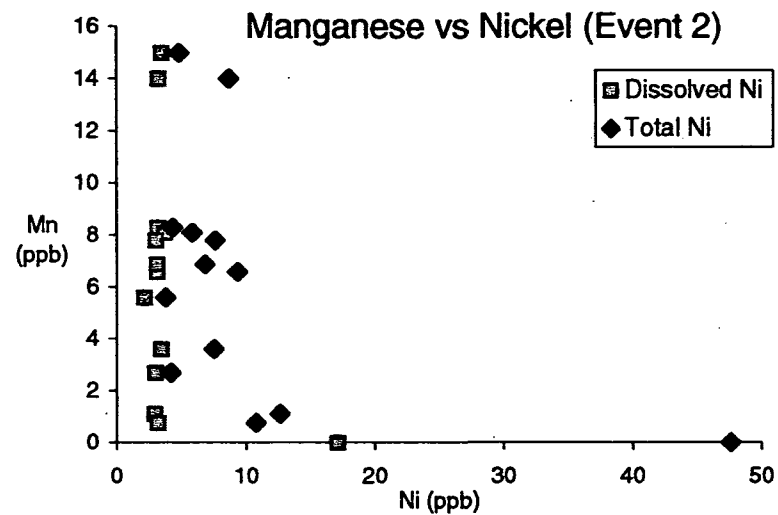
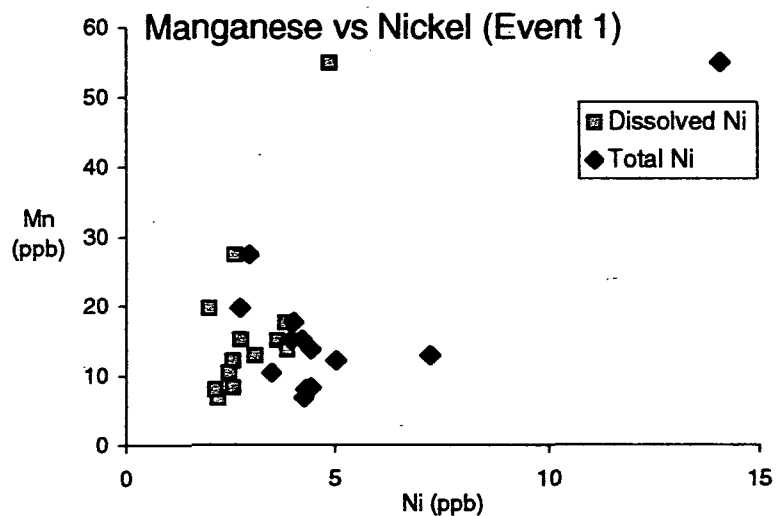
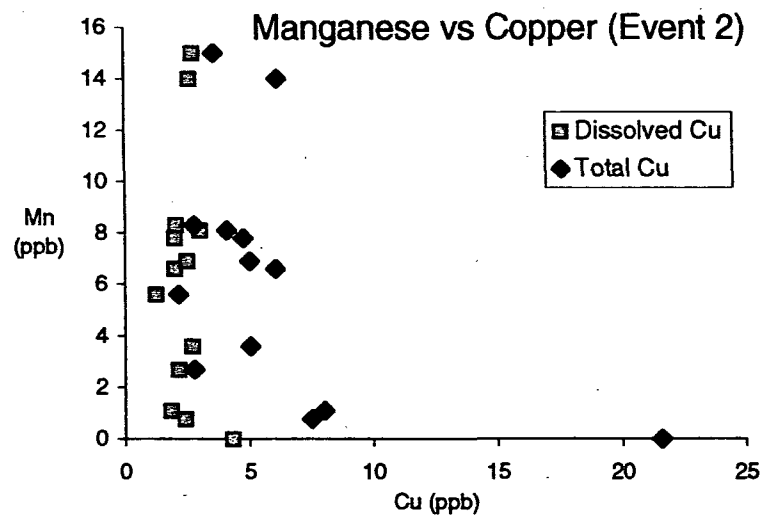
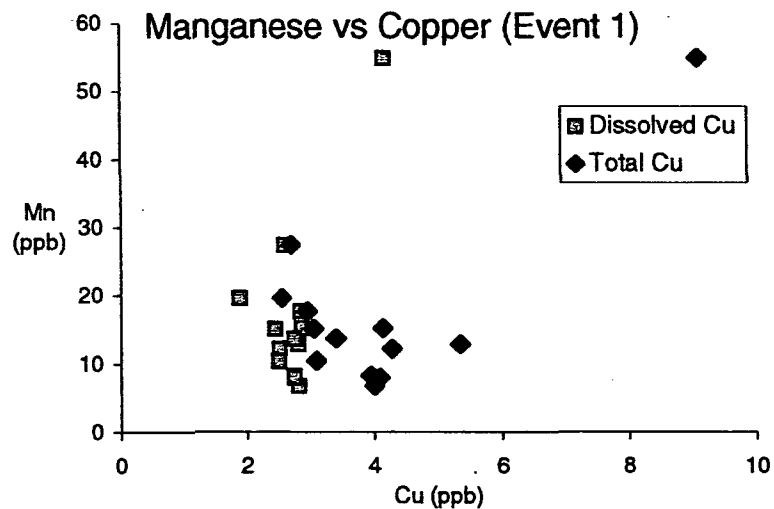


Dissolved

	WER Event 1	WER Event 2
BA40	2.70	4.19
BB15	2.41	3.24
LCB01	2.50	4.66
LCB02	2.41	5.18
BB30	2.52	3.47
BC10	2.21	2.57
BD20	2.19	2.55
SPB01	2.01	2.61
BD15	2.70	5.32
SPB02	1.71	3.19
SPB03	1.75	2.46
BF10	2.54	3.51
BF20	1.69	3.18







Event 2

