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SUBJECT: Update on Sampling Events 1, 2 and 3 – Copper Nickel Impairment Assessment - North of Dumbarton Bridge

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The following is an update of information regarding the first three sampling events of the Copper and Nickel study North of Dumbarton Bridge as described in the "Work Plan for Copper and Nickel Impairment Assessment to Assist in Preparation of the 2002 303(d) List." To date, three of four sampling events have been completed successfully. The fourth and final event is tentatively scheduled for June 2001. The data summarized in this report pertain to the first two events (September 2000 and February 2001). The data from the third event (April 2001) are not yet available.

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Scatter Plots:

Introduction

San Francisco Bay exceeded the 1986 Basin Plan objectives and/or USEPA national criteria for copper and nickel. These exceedances raised concern about copper toxicity to sensitive organisms in the Bay. However, toxicity is also dependent on other water constituents such as pH, hardness, suspended solids, dissolved carbon compounds and salinity. Water quality objectives do not take into account these variables and may be overly protective for the ambient water in the Bay. A water effect ratio (WER) can be used to compare the toxicity of site water to the toxicity of laboratory water. The USEPA believes that a WER appropriately takes into account the site-specific toxicity of the metal (copper) and synergism, antagonism and additivity with other constituents of the site water. Indicator organisms (*Mytilus edulis*) are introduced to laboratory and site waters that have been spiked with known concentrations of copper. The WER is found by dividing the dissolved copper EC_{50}[1] of the water collected at the site by the dissolved copper EC_{50} of the laboratory water. It is believed that when the WER is greater than 1.0, the site water actually reduces the toxic effects of copper.

A work plan was drafted in August 2000 describing studies that could be used 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. Initial samples were collected on August 30, 2000 in both shallow and deep-water sites in San Pablo Bay to determine the appropriate dilution range for laboratory bioassay testing. Sampling sites were selected to show spatial trends and hydrodynamic influences throughout the North and Central Bays (Table 2). The transects were chosen to provide information regarding conditions in the shallow areas of San Pablo Bay and the Central Bay shoals. Models suggest that there is a copper concentration gradient from the deep channel to the mudflats in San Pablo Bay. To date, three of four proposed sampling events (2 summer, 2 winter) have been completed.

Sampling Conditions

Clean sampling techniques were used for all fieldwork. Site water was collected by pumping (peristaltic) water into 5-gallon acid-rinsed cubitainers at slack high tide to minimize TSS and DOC concentrations. Samples were placed on ice immediately after collection for transport to the laboratory. Each of the events thus far was chosen on different criteria (Table 1).

Table 1 – Sampling Conditions

Event	Dates	Conditions	Delta Outflow (cfs)	
			Day 1	Day 2
1	9/5/00 9/7/00	"glassy" water; a representation of fall, dry season conditions.	8,292	6,161
2	2/13/01 2/15/01	Relatively turbid conditions; a representation of winter, wet season conditions.	19,029	20,853
3	4/22/01 4/24/01	Scheduled to coincide with South Bay stratified conditions that typically precede a phytoplankton bloom	20,915	20,909

[1] Concentration of dissolved copper at which 50% of test organisms are adversely affected

Range finding trip was very windy with a little rain. Samples were high in suspended solids.

Table 2 – Sampling Locations and Dates Sampled for Events 1-3

Site Code	Site Description	Date Sampled		
BD15	Petaluma River	9/5/00	2/13/01	4/24/01
BD20	San Pablo Bay			
SPB01	Shallow area between BD15 and BD20			
SPB02	Shallow area in eastern SPB; mid-point on transect			
SPB03	Shallow area in eastern SPB; near shore on transect			
BF20	Grizzly Bay – *estuarine conditions but close to Delta*			
BF10	Pacheco Creek			
BC10	Yerba Buena Island	9/7/00	2/15/01	4/22/01
BB30	Oyster Point			
BB15	San Bruno			
BA40	Redwood Creek			
LCB01	Shallow area in Central Bay (mid-point on transect)			
LCB02	Shallow area in Central Bay (near shore on transect)			

Laboratory Conditions

Measurements of temperature, pH, dissolved oxygen (DO) and salinity were made in the field. Upon arrival at the laboratory, the water quality (hardness, alkalinity, total suspended solids (TSS), ammonia) of the samples from each site was measured. Trace metal analyses were conducted by Frontier GeoSciences in Seattle, Washington using a Co-APDC coprecipitation extraction[2]. Following filtration (0.45 um) for dissolved samples, copper and nickel samples were preserved to pH 1.8 and dissolved manganese samples were preserved to 1% (v/v), all with nitric acid. The results of these chemical analyses were reviewed for measurements that were outside of reasonable limits (i.e., dissolved value greater than total value) and re analyzed if necessary. Analyses for copper, nickel, manganese and hardness were performed using ICP-MS[3]. Total organic carbon (TOC) and dissolved organic carbon (DOC) analyses were subcontracted to Analytical Resources, Inc. (ARI) in Seattle, Washington (EPA Method 415.1) [Event 1] and EN CHEM, Inc. in Madison, Wisconsin (Method SW846 9060) [Event 2]. Clean techniques were used in all laboratory work.

The WER procedure recommends that initial and final copper measurement be made on all concentrations used in determining the endpoint. Only initial total and dissolved copper measurements were made for selected concentrations and the control. Statistical analyses and WER calculation were based only on measured copper

[2] Cobalt(II) – ammonium pyrrolidinedithiocarbamate (APDC) coprecipitation extraction removes the analytes of interest from the sample matrix and preconcentrates the sample to allow for lower detection limits.

[3] Using EPA Draft Method 1638: Inductively Couple Plasma – Mass Spectrometry (ICP-MS)

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 was run for Event 1 in which both initial and final values were 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 (Table 3).

Table 3 - Copper Concentrations (ppb) Before and After Toxicity Testing (Event 1)

Nominal Spike	Dissolved		Total	
	Initial	Final	Initial	Final
0	2.86	2.83	2.97	3.05
16.7	15.6	13.4	19.5	18.3
24	20.8	19.7	26.7	23.8
34.3	29.6	26.2	36.9	31.0

To remove potential predators in the toxicity test, all site-water samples were passed through a 50 um filter screen. Toxicity tests were conducted at the ambient salinity of the collected laboratory water (30-32ppt). This necessitated the "salting up" of some samples. In Event 1, samples from the Central Bay met this criterion as collected, but most samples from the North Bay were well below this level and artificial salts were added to bring them to the proper salinity. In Event 2, all samples required the addition of artificial salts to bring them up to the proper salinity. Lab water from Granite Canyon Marine Pollution Studies Laboratory was filtered to 0.45 μm before use in the tests.

Site water was spiked with several concentrations (5-9 dilutions) of copper in a 0.7 dilution ratio for toxicity testing. Tests were conducted using 5 replicates of 10mL of each of the concentrations in a scintillation vial inoculated with fertilized *Mytilus edulis* embryos at or beyond the 2-celled stage. Vials were incubated for 48 hours at 15°C (±1°C) and then the number of normal D-shaped, straight hinged larvae was counted. Once toxicity testing was complete, EPA guidance criteria were used to choose water samples for chemical analysis. The EPA guidance called for analysis of:

- Samples in which some, but not all, of the test organisms were adversely affected
- The highest concentration that did not adversely affect any test organisms
- The lowest concentration that adversely affected all of the test organisms
- The controls

Using these criteria, rather than having all the toxicity test samples analyzed was more cost effective because 30 samples were exempt from analysis. However, waiting until the completion of the toxicity testing before sending samples to Frontier GeoSciences for analysis resulted in an approximately one month delay for final results. These tests were performed to develop dissolved copper WERs at each of the 13 sampling sites (Table 4). The WER was found by dividing the EC_{50} of the water collected at the site by the EC_{50} of the laboratory water.

Table 4: Dissolved Copper[4] and Dissolved Copper WERs

Site	Dissolved Copper (ppb)		Dissolved Copper WER	
	Event 1	Event 2	Event 1	Event 2
BA40	2.86	2.74	2.70	4.19
BB15	2.88	2.07	2.41	3.24
LCB01	2.45	2.70	2.50	4.66
LCB02	2.76	3.02	2.41	5.18
BB30	2.60	2.15	2.52	3.47
BC10	1.89	1.26	2.21	2.57
BD20	2.51	1.85	2.19	2.55
SPB01	2.52	2.42	2.01	2.61
BD15	**4.17**	**4.31**	2.70	5.32
SPB02	2.82	2.01	1.71	3.19
SPB03	2.76	2.01	1.75	2.46
BF10	2.83	2.50	2.54	3.51
BF20	2.76	2.63	1.69	3.18

BOLD values indicate those samples that exceeded the CTR chronic criterion for dissolved copper.

Schematic maps of San Francisco Bay were made to show the preliminary spatial variations in dissolved copper WERs, dissolved copper, dissolved nickel and salinity. Shaded values represent the shallow water sites. Bar graphs were made to portray WERs, total and dissolved copper, total and dissolved nickel, salinity, TSS, alkalinity, TOC and DOC in the North and Central Bays. Reading from left to right, the sites are plotted from south to north and then west to east, starting in the Central Bay . On the TOC/DOC bar graph for Event 1, there are 3 DOC bars missing (BC10, BB30, BB15) because the DOC concentrations at these sites were all non-detect (<1.5 mg/L). Scatter plots were made using combinations of WER, TOC, DOC, total and dissolved metals, salinity and TSS. Lines through the total metal vs. TSS data appear to show a strong linear correlation between the two; however these are only preliminary findings.

QA/QC

Quality Assurance and Quality Control were implemented in this study in the form of duplicates, laboratory blanks, field blanks, procedure blanks, method blanks and unsalted samples. Duplicates showed good reproducibility (Table 5). All blanks showed reasonable similarity (Table 6). All toxicity tests showed appropriate affects (i.e., low copper concentration did not affect organisms, high copper concentration affected all organisms).

[4] The California Toxics Rule (CTR) criteria for dissolved copper is 3.1 µg/L

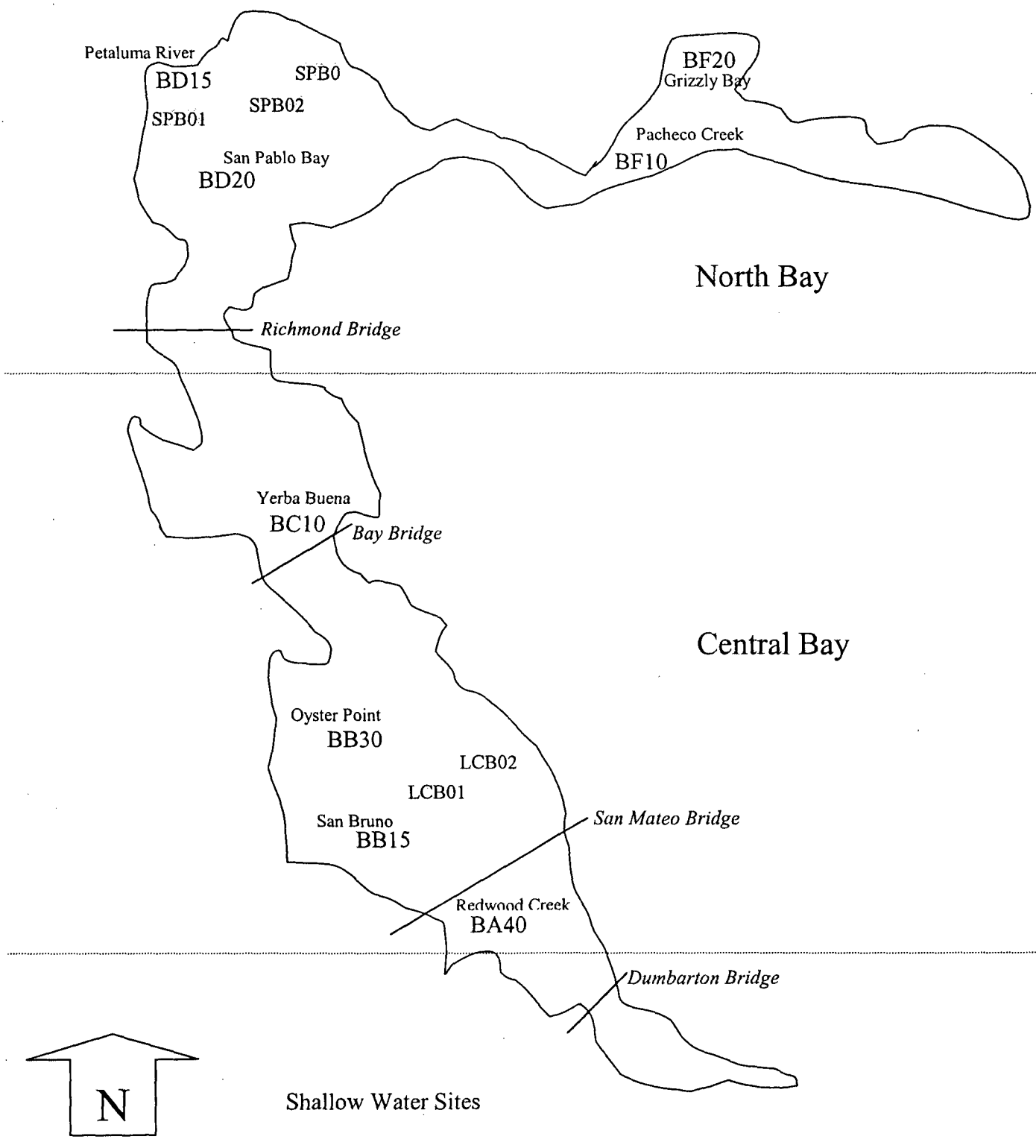
Table 5 – Comparison of Samples and their Duplicates for Dissolved and Total Copper (ppb)

Event	Site (nominal spike)	Dissolved		Total	
		Actual	Duplicate	Actual	Duplicate
1	BA40 (0)	2.86	2.71	2.97	2.97
1	BC10 (24)	19.4	19.9	26.8	25.9
1	BD15 (0)	3.00	3.08	7.23	7.92
1	BF10 (0)	1.94	2.03	3.00	3.13
1	LW (11.8)	10.3	10.2	12.7	11.5
1	BD20 (0, no salt)	2.51	2.56	3.11	3.49
1	BD20 (0, salt)	0.40		2.43	
2	SPB03 (raw)	2.01	1.81	4.77	4.33

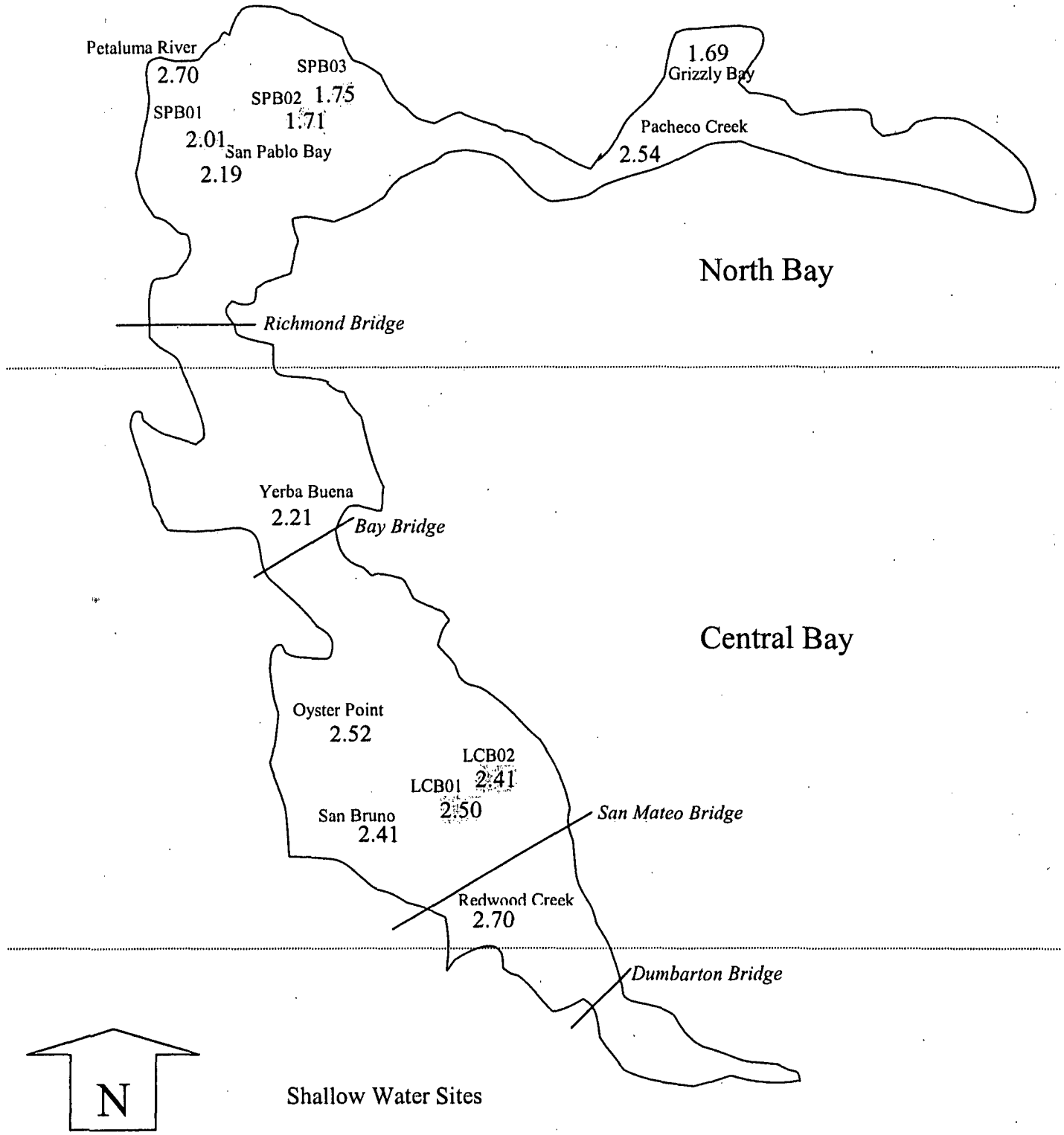
Table 6 – Comparison of Copper Blanks (ppb)

Type of Blank	Event	Dissolved	Total
Blank	1	0.62	0.65
	2	<0.02	<0.02
Field	1	0.71	0.77
	2	0.01	0.01
Laboratory	1	0.71	0.72
	2	<0.01	<0.01
Procedure	1	0.88	1.01
	2	<0.02	<0.02

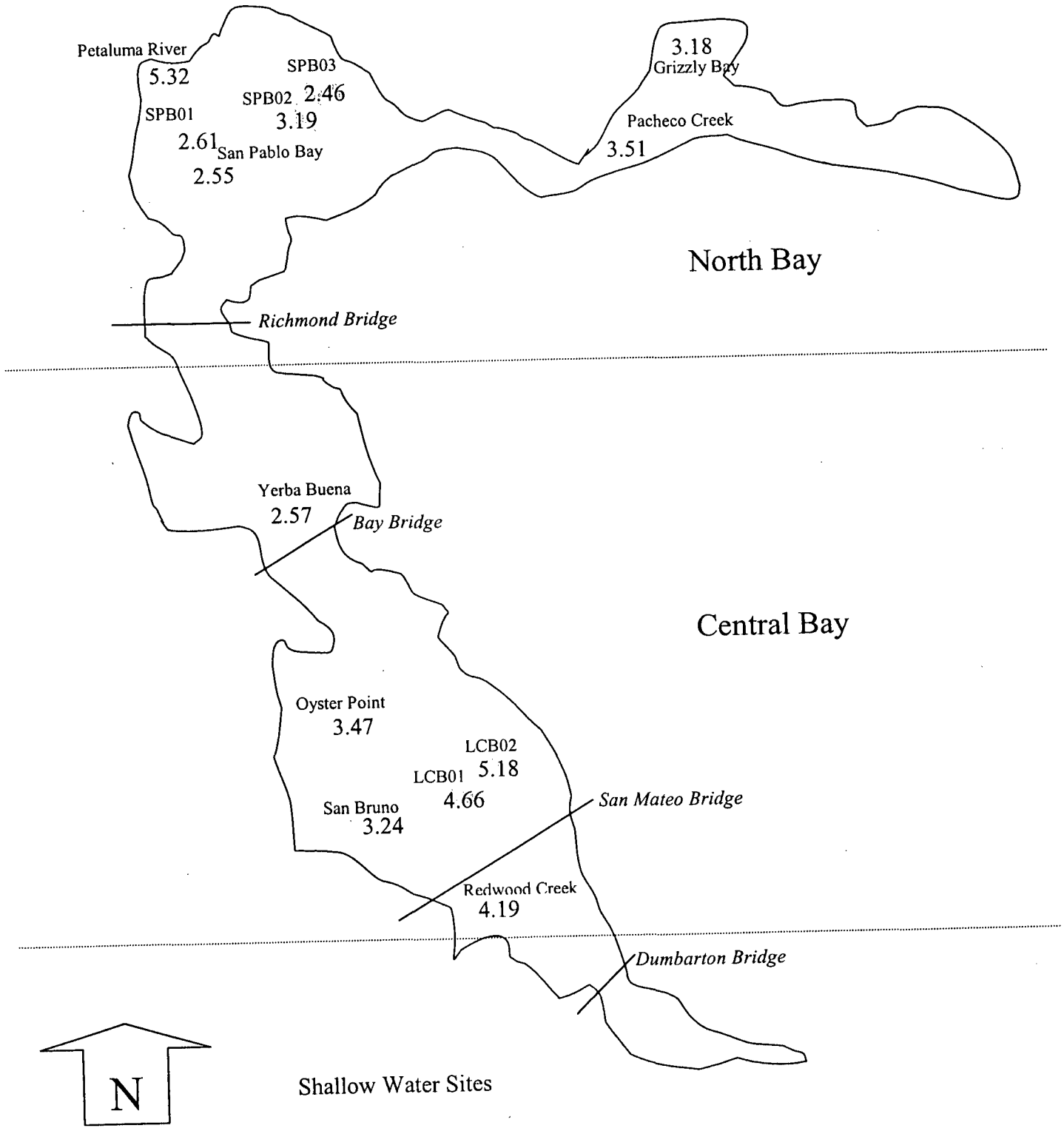
Sampling Sites



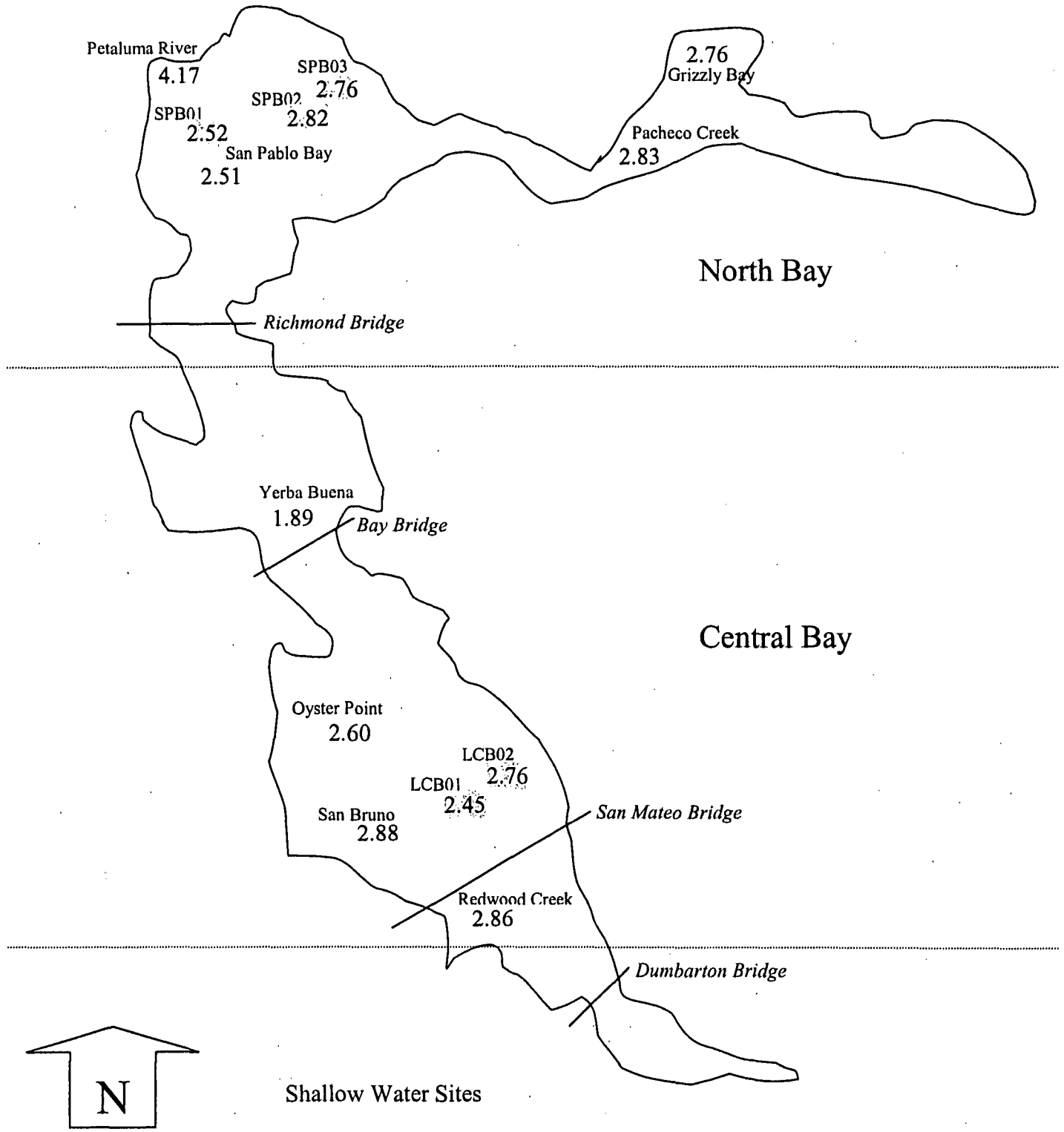
Dissolved Copper WERs - Event 1



Dissolved Copper WERs - Event 2



Dissolved Copper (ppb) - Event 1



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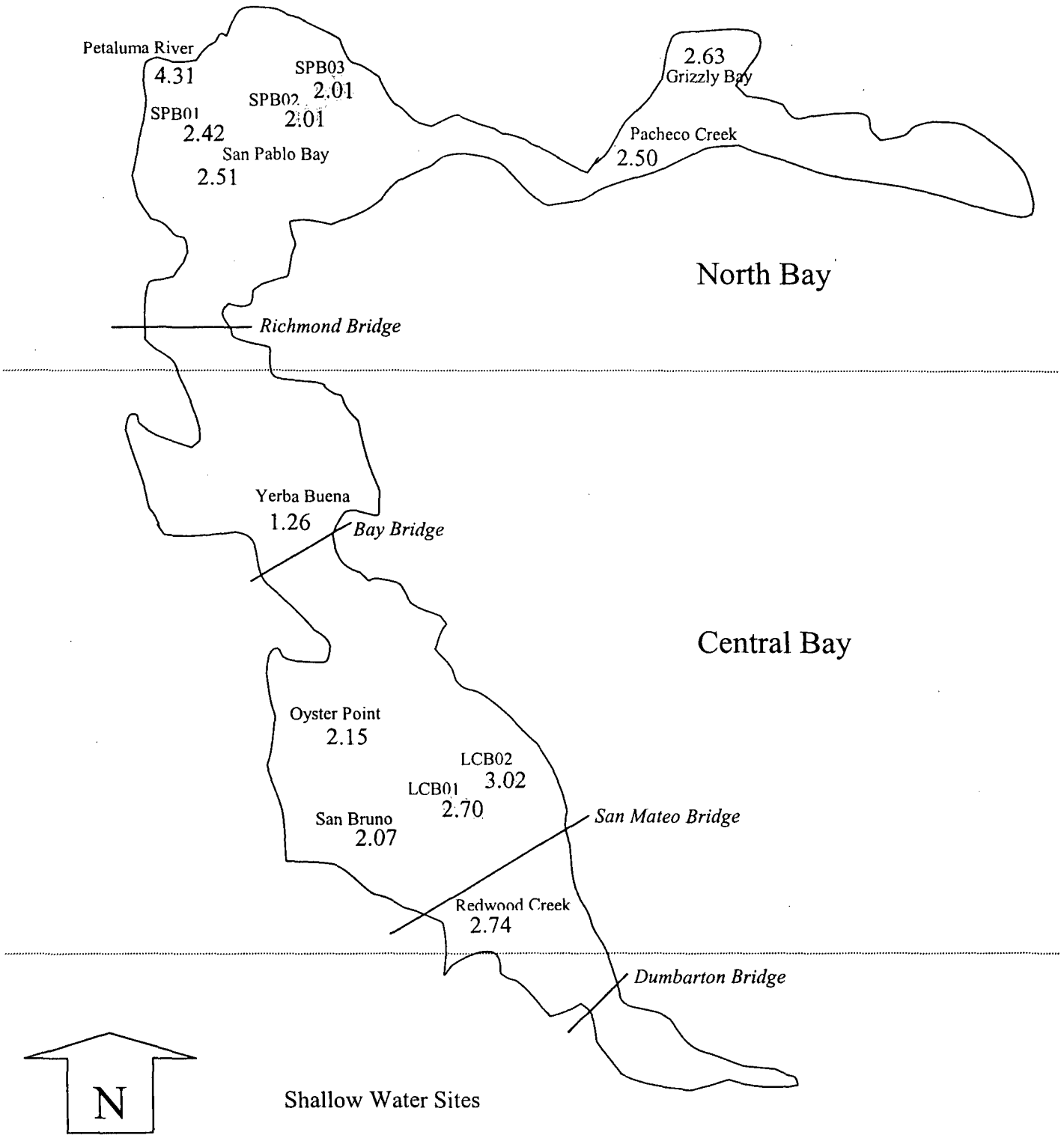

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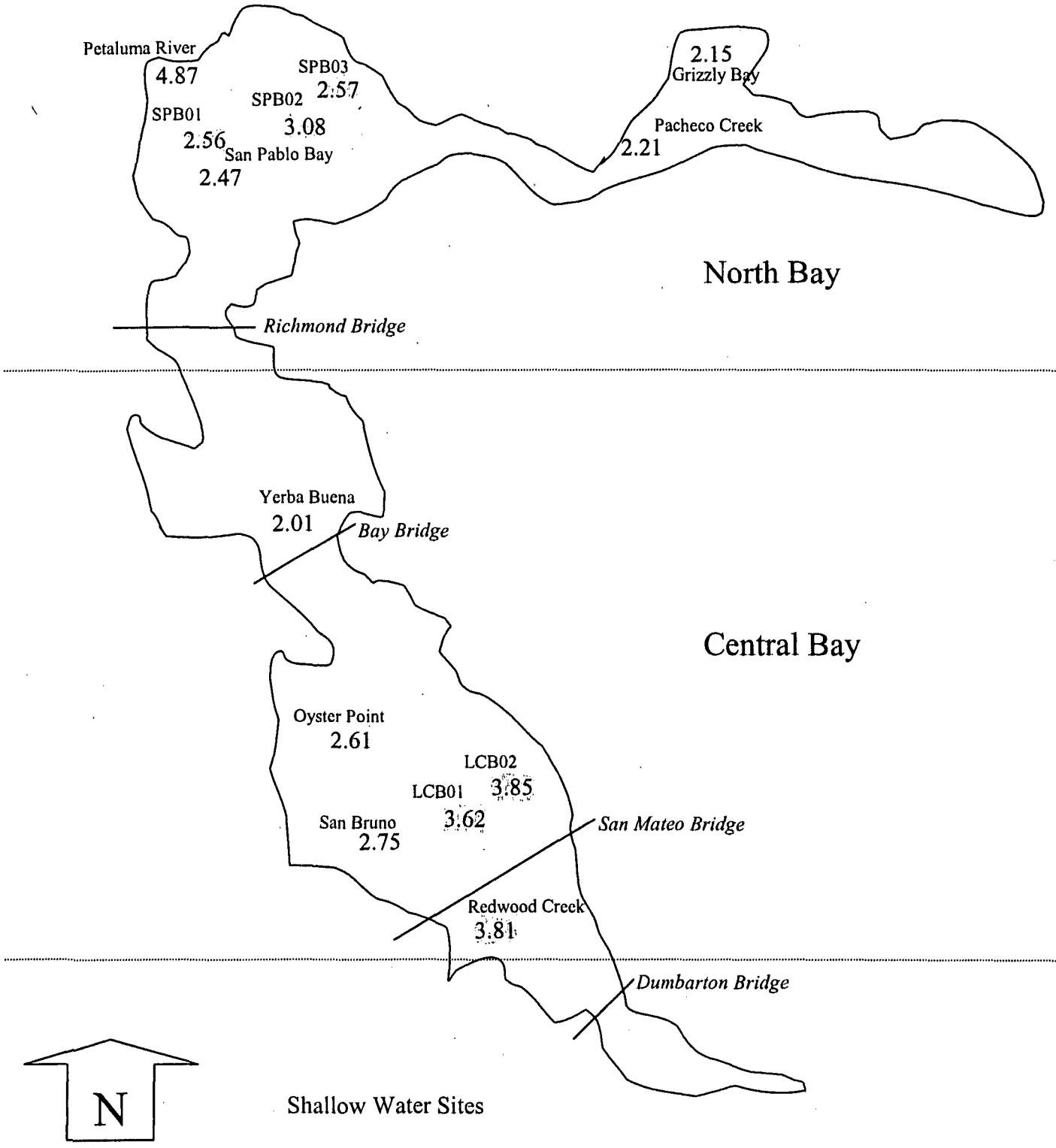

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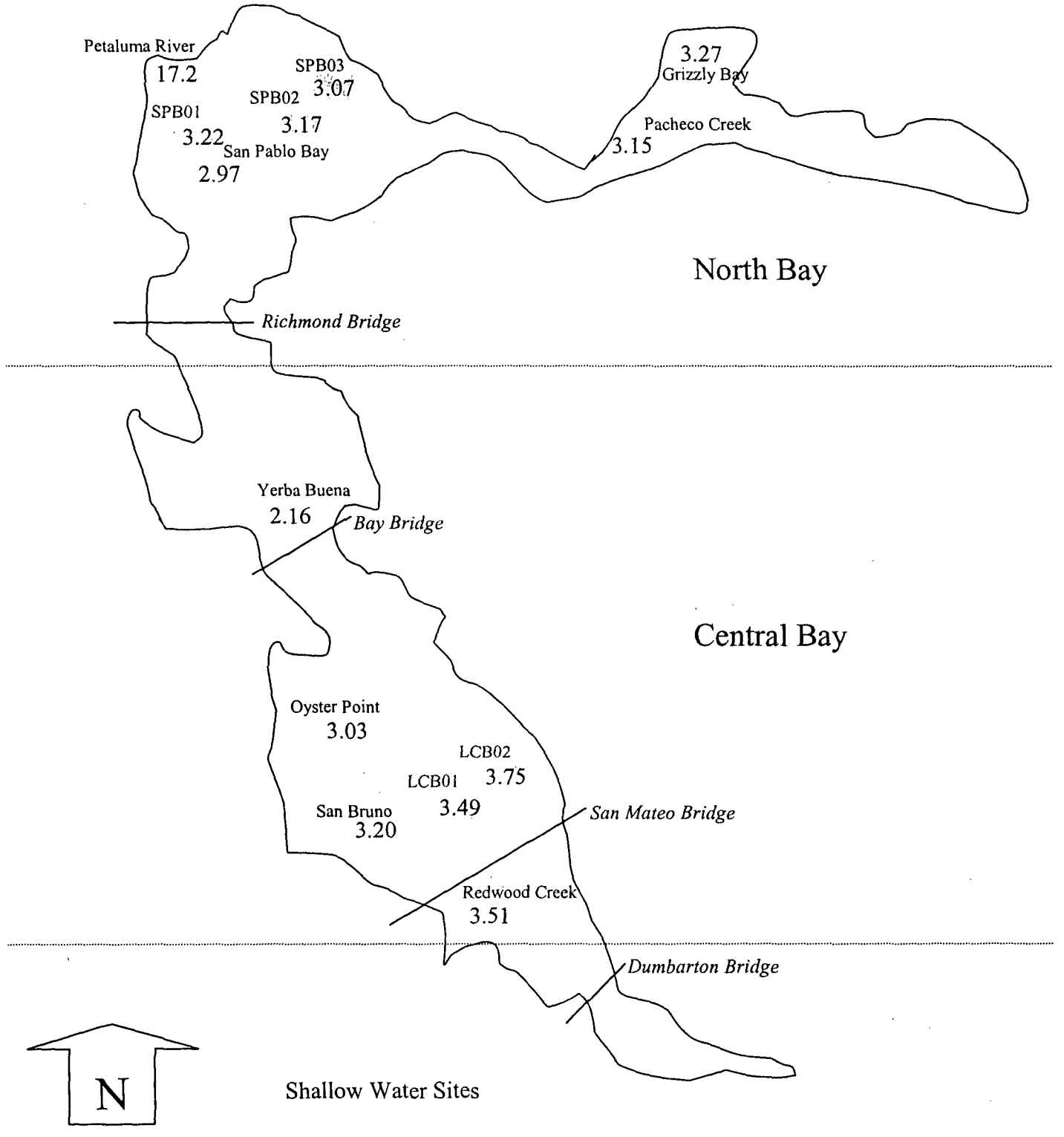
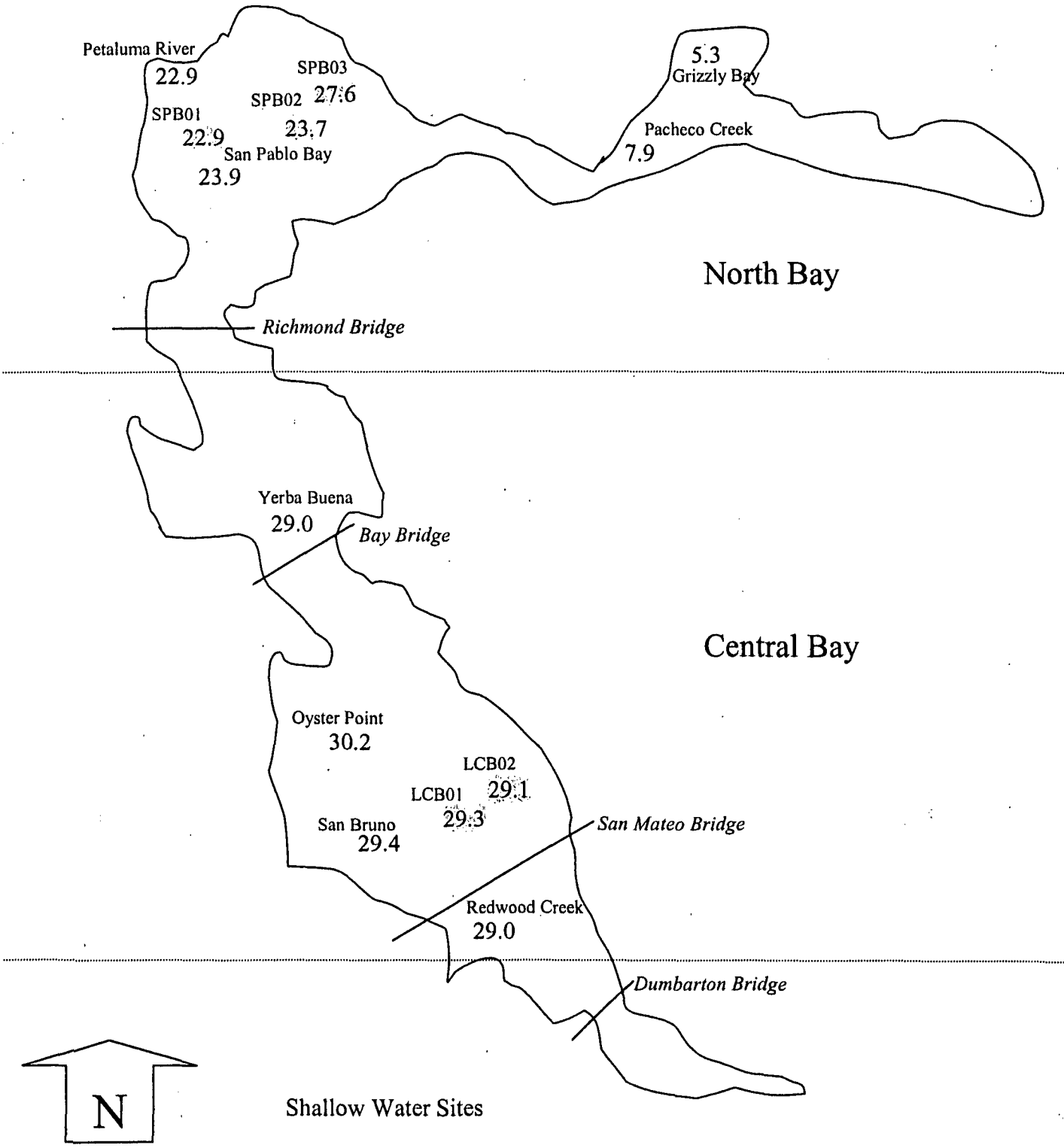


Salinity (ppt) - Event 1



Salinity (ppt) - Event 2