Part E—Metals (Cadmium, Copper, Lead and Zinc)

Introduction

This section of the TMDL presents an analysis of the major sources of heavy metals to water bodies of Newport Bay. Information is compiled to develop TMDLs for cadmium in San Diego Creek and Upper Bay only, and for copper, lead and zinc in all waterbodies of Newport Bay including Rhine Channel. The source analysis summarizes monitoring results to provide a preliminary assessment of metal distribution relevant to water quality problems. Although many metals analyses have been completed in all media (water, soil and fish tissue), including toxicity tests which implicate metals as toxicants, no study has been completed to date that clearly establishes the source of any specific metal. Heavy metals are generally attributed to surface runoff from open space and urban areas; yet some metal inputs come from other sources such as nurseries and other agricultural applications within the watershed as well as recreational boat hulls (for copper).

This technical support document (TSD) begins by describing the chemical characteristics of each heavy metal, including aqueous behavior in natural waters. Next monitoring results for each metal in all waterbodies are reviewed and where feasible conclusions are included. Unfortunately, water column sampling methods were not consistent and quality control and quality assurance measures not uniformly completed, so there are some limitations in comparing and interpreting these surface water results. Descriptions and estimates of background sources (natural runoff and ambient seawater) and miscellaneous sources (e.g., copper from boat hulls, nursery applications and direct atmospheric deposition) are included.

The final section of this TSD explains methods used for calculating dissolved metal loads for each water body. This includes methods for determining dissolved metal loadings via the flow-based approach for San Diego Creek as well as the approach for approximating the Newport Bay loading capacity.

I. Physicochemical description of metal toxicants

Copper and Zinc are essential elements for all living organisms but elevated levels may cause adverse effects in all biological species. Cadmium and Lead are presumed to be non-essential elements for life; more importantly, even at extremely low environmental concentrations these elements may create adverse impacts on biota. In fact molecular biology studies have demonstrated that Cd and Pb atoms may substitute for other divalent metals such as Cu and Zn within enzyme binding sites. Biochemical similarities between these atoms suggest that Cd and Pb may also compete with cell surface uptake sites or bind to sulfur and nitrogen donor atoms of various functional groups within the cell. This is more likely to occur in freshwater systems (where dissolved calcium can be low) than in saline water since calcium ameliorates divalent metal toxicity (Playle and Dixon 1993).

Dissolved metals are directly taken up by bacteria, algae, plants, and planktonic and benthic organisms. Dissolved metals can also adsorb to particulate matter in water column and enter aquatic organisms through various routes. Cadmium, copper, lead and zinc may bioaccumulate within lower organisms, yet they do not biomagnify up the food chain as do mercury and selenium (Moore and Ramamoorthy 1984). Of all of these metals, copper is considered the most potent toxin at environmentally relevant aqueous concentrations. Copper is generally more toxic to lower aquatic organisms such as phytoplankton, copepods and ciliates than to birds or mammals because the higher animals seem capable of regulating copper concentrations in tissues (USF&W 1998). Copper is more commonly found in herbivorous fish than carnivorous fish from the same location (USF&W 1998). Copper is used as an aquatic herbicide to reduce algae growth in reservoirs and also applied (via antifouling paints) to boat hulls in marinas.

Importance of speciation in natural waters

The fate and transport of metals in natural waters is influenced by the physical state and chemical complexation of each element. Physical separation methods (i.e., filters) define metals associated with the particulate, colloidal or dissolved phases. Unfiltered or “total” metal samples represent the sum of all size fractions; whereas filtered or “dissolved” samples yield metals in solution. As a general rule, particulate metal concentrations are higher than those in dissolved phase for all metals in these TMDLs. This is based in part on the inherent reactivity of negatively charged particulate matter and positively charged metal ions (Buffle 1989). As outlined in the California Toxics Rule, EPA has defined aquatic life water quality criteria for these metals based on the dissolved fraction of aqueous samples (EPA 2000a); these serve as numeric targets for these TMDLs.

Within the dissolved fraction, metals exist in various chemical forms or species (Buffle 1989). Each divalent metal may exist by itself as the free metal ion (e.g., Cu^{++}) or it may combine with other elements to form inorganic complexes such as other hydroxyl or chloride chemical species (e.g., $CuOH^+$ and $Cu(OH)_2$ or $CuCl^+$ or $CuCl_2$). Metal-organic forms may also exist dependent on presence of soluble matter such as synthetic chelators, phytoplankton exudates, humic and fulvic acids and other forms of dissolved organic carbon. Metals change chemical forms in freshwater based on pH, temperature, oxygen, organic matter, and biological activity; toxicity is affected likewise. In general, acidic soft freshwaters demonstrate high toxicity to aquatic organisms due to elevated concentrations of free metal ions (e.g., Cu^{++}), the most bioavailable forms. By contrast, slightly alkaline hard freshwaters contain free calcium (Ca^{++}) and magnesium (Mg^{++}) ions to ameliorate divalent metal toxicity. In seawater systems, aquatic chemists have discovered much more metal bound up in organic complexes as compared to inorganic complexes (Bruland *et al.* 1994). For example within estuarine systems dissolved copper results appear to contain 90 to 99% organic complexes, consequently free copper ion concentrations are ca. 100 fold lower than dissolved copper concentrations (Donat *et al.* 1994). Similar results have been estimated for Pb (70 to 95%), Zn (50 to 97%) and Cd (70 to 80%) (Muller 1996, Kozelka and Bruland 1997). Organic complexation in freshwater systems exists and presumably at lower levels in flowing systems than relatively static ones. For primary producers such as phytoplankton, ciliates, copepods, and crab larvae, bioavailability is generally correlated to the free metal ion concentration, thus toxicity is much lower in seawater systems than in freshwater bodies (Sunda et al. 1987).

Sediments contain particulate sorbed metals, often referred to as bulk sediment concentrations. Interstitial porewaters of sediments also contain metals. Such porewaters may contain acid-volatile sulfides in concentrations higher than the combination of certain metals (Cd, Cu, Pb, Ni, Zn) and render that portion unavailable and non-toxic to biota (Di Toro et al. 1992).

II. Monitoring Results

Surface waters

In the past five years, three separate studies have compiled heavy metals monitoring data for freshwater bodies of Newport Bay. Below is a brief review of each study and some comments about sampling techniques relevant to comparisons to water quality standards. As previously noted, it is difficult to make direct comparison of water measurements since quality assurance and quality control was not consistent across each study. A summary of monitoring results for each dissolved metal by waterbody is provided in Tables E -- 1(a - d).

IRWD monitoring data

From Dec. 1997 to March 1999, Irvine Ranch Water District monitored 2 stations on bi-monthly basis. In general results include both wet weather and dry weather conditions, although sampling plan did not target to collect runoff from individual storms. Individual grab samples were collected using trace metal clean techniques and filtered in the laboratory prior to analysis. Thus results are best interpreted as single snap shots of water quality in San Diego Creek and can be compared only to acute (hardness dependent) water quality standards.

319(h) monitoring data

Lee and Taylor (2001a) collected grab samples at 10 sites covering San Diego Creek and Santa Ana-Delhi Channel during three storms and one dry weather event in 2000. Trace metal clean techniques were used; however, hydrographs with indicated collection times (figures A2-8, A3-8, A3-9 therein) reveal samplers missed peak flow conditions. This study provides a decent spatial assessment of metal inputs during slightly elevated flows (ca. 200 cfs). Maximum concentrations for all three metals occur in Santa Ana-Delhi Channel, followed by Costa Mesa Channel and Hines Channel. The authors suggest that elevated concentrations in Hines Channel relative to concentrations measured downstream in San Diego Creek at Campus can be attributed to dilution as more water enters the tributary system from various channels.

OCPFRD monitoring data

Orange County Public Facilities Resource Division (OCPFRD), part of Orange County Environmental Management Agency, has been collecting water samples in the watershed for more than 15 years. For the purposes of developing this TMDL, EPA focused on recent results (past five years), which included monitoring data representing a wide range of flow conditions (i.e., 1998 was an exceptionally high water year due to El Nino conditions and 1999 was a normal water year as discussed more in Technical Support Document - Part B). Total and dissolved results, along with hardness values, for each sampling event were reported in the annual report for the NPDES stormwater permit (OCPFRD 2000). OCPFRD monitoring plans require several (minimum of five) composite samples collected each day over the course of each storm event; as well as grab samples collected throughout the hydrograph during the first flush event of each water year. Dry weather samples are individual grabs. OCPFRD staff to date has not used trace metal clean sampling techniques. Paired data from unfiltered (total metals) and filtered (dissolved metals) provides preliminary evaluation of metal translator values. These translator values were close to 1.2 and therefore we assumed dissolved metals are 80% of the total recoverable results. In addition to summary results presented in Tables E-1(a - d), noteworthy results include: elevated Cu in Lane Channel, Bonita Canyon Channel and Costa Mesa Channel, high Pb in Lane Channel and high Zn in Costa Mesa Channel.

Table E-1a. Dissolved Copper Monitoring Results by Waterbody (ug/L)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median
San Diego Creek	1996-00	OCPFRD	91	2.1	100	16.4 ± 14	14.0
	1997-99	IRWD	32	1.7	35.8	13.0 ± 10	12.8
	2000	Lee and Taylor	4	2.4	5.5	3.8	3.5
Santa Ana Delhi	1996-00	OCPFRD	65	9.3	74	22.2 ± 12	18.1
	2000	Lee and Taylor	3	5.0	6.3	6.4	6.3
Upper Bay	1996-00	OCPFRD	83	3.4	29.0	11.0	11.0
	1997-99	IRWD	10	1.2	2.3	1.7 ± 0.4	1.7
Lower Bay	1996-00	OCPFRD	25	8.2	26.3	15.9	16.1
	1997-99	IRWD	6	0.6	3.4	2.3 ± 0.9	2.3

Table E-1b. Dissolved Lead Monitoring Results by Waterbody (ug/L)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median
San Diego Creek	1996-00	OCPFRD	90	1.0	70	4.9 ± 10.6	2.0
	1997-99	IRWD	26	0.01	5.1	1.01	0.18
	2000	Lee and Taylor	4	0.05	0.35	0.19 ± ? ?	0.11
Santa Ana Delhi	1996-00	OCPFRD	64	1.0	45	5.3 ± 7.4	2.0
	2000	Lee and Taylor	3	0.03	0.95	0.63	0.90
Upper Bay	1996-00	OCPFRD	83	<2	<20	3.1	2.0
	1997-99	IRWD	10	0.023	0.96	0.44	0.29
Lower Bay	1996-00	OCPFRD	25	<2	<2	<2	<2
	1997-99	IRWD	6	0.03	0.89	0.45 ± 045	0.43

Table E-1c. Dissolved Zinc Monitoring Results by Waterbody (ug/L)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median
San Diego Creek	1996-00	OCPFRD	86	5.2	640	46.6 ± 81.9	16.5
	1997-99	IRWD	38	3.5	106	13.7 ± 16.7	12.0
	2000	Lee and Taylor	4	2.6	23.1	13.1	8.2
Santa Ana Delhi	1996-00	OCPFRD	59	10.0	532	95.0 ± 102	57.4
	2000	Lee and Taylor	3	5.4	35.9	31.8	27.7
Upper Bay	1996-00	OCPFRD	83	10	100	19.9	14.5
	1997-99	IRWD	23	2.5	11.5	6.8± 3.1	5.5
Lower Bay	1996-00	OCPFRD	25	8.2	29.5	17.3	16.3
	1997-99	IRWD	13	1.1	44.4	10.6 ± 10.1	7.5

Table E-1d. Dissolved Cadmium Monitoring Results by Waterbody (ug/L)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median
San Diego Creek	1996-00	OCPFRD	88	0.5	18	1.7 ± 2.7	1.0
	1997-99	IRWD	32	0.13	0.65	0.31 ± 0.12	0.30
	2000	Lee and Taylor	4	0.13	0.27	0.22	0.20
Santa Ana Delhi	1996-00	OCPFRD	63	<1.0	10.0	1.6 ± 2.9	1.0
	2000	Lee and Taylor	3	0.08	0.14	0.12	0.10
Upper Bay	1996-00	OCPFRD	83	<1.0	<10	1.6 ± 2.2	1.0
	1997-99	IRWD	10	0.095	0.22	0.14 ± 0.04	0.13

Sediments

Sediment monitoring results for both fresh and saltwater bodies are summarized in Tables E-2(a - d). Individual results were compared with sediment quality guidelines appropriate for each water body type; freshwater and saltwater threshold effect levels (TEL) and saltwater probable effect levels (PEL). These TEL and PEL values are from Florida Dept. of Environmental Protection study (MacDonald et al. 1996). Some freshwater sediment metal results within San Diego Creek are above TEL values, most notably Cd. But rarely, if ever, do the sediment metal levels exceed PEL values (OCPFRD 2000). No doubt during heavy storm events, Cd, Cu, Pb and Zn contaminated sediments are transported from freshwater bodies to saltwater bodies in Newport Bay; however, we do not anticipate much dissolved metal fluxes from these freshwater sediments into the San Diego Creek water column.

In saltwater bodies of Newport Bay, some sediment metal concentrations are elevated relative to TEL values. The higher frequencies of exceedances of TEL values occur in Lower Newport Bay and Rhine Channel. Maximum values always occur in Rhine Channel, especially for copper, which frequently (80%) exceeds the PEL value. This observation supports the theory that fluvial transport along the freshwater/saltwater gradient produces higher sediment metal concentrations where sediment deposition is most likely to occur.

Within each water body, sediment metal concentrations fluctuate widely and there is no systematic increase or decrease from long-term trend analyses. Part of this may be attributed to the patchy nature of sampling sediments via grabs as well as the presumption that sediments and associated contaminants shift during major storms. Based on spatial distribution of these bulk sediment chemistry results, one can generalize that metal concentrations are low in freshwater bodies and systematically increase along the saltwater gradient. (Cadmium appears to have contrasting distribution between fresh and saltwater.) Another pattern does exist within Lower Bay, metal sediment concentrations decrease along the west to east gradient. That is, the lowest values occur near Newport Jetty closest to open ocean waters. Maximum levels exist in Rhine Channel, which is not surprising given poor tidal flushing and long residence times (up to 9 days) within this dead-end reach (RMA 2001).

AVS/SEM and porewater results

Two other studies -- BPTCP (1997) and Bight '98 (SCCWRP in prep.) assessed relevant sediment metal parameters. In 1996, BPTCP measured acid-volatile sulfides (AVS) and simultaneously extracted metals (SEM) at one site in Rhine Channel. The SEM total was greater than AVS total (6.80 vs. 4.65) with SEMCu about 68% of SEM total value. As part of Bight '98, AVS/SEM and interstitial porewater concentrations were measured at 11 Lower Bay sites, excluding Rhine Channel. Since all 11 sites showed consistent results -- AVS totals were greater than SEM totals, one could assume the metals were bound to acid-volatile sulfides. However at half the sites, individual porewater concentrations showed elevated Cu concentrations relative to saltwater chronic CTR value (3.1 ppb), with two sites showing 33.3 ppb and 65.9 ppb. Porewater concentrations for Pb and Zn were below saltwater chronic values, 8.1 ppb and 81 ppb respectively.

In summary, San Diego Creek and Upper Bay sediment metals are not frequently above TEL values, except for Cd. We presume these sediments do not release metals into the water column, rather these sediments are a trap for particulate metals from the water column, thus acting as a sink. This appears to be true for Cd, Pb and Zn in Lower Bay, where porewater concentrations are low. However in the case of copper both sediment bulk levels and interstitial porewater concentrations are elevated. Therefore, benthic fluxes, both resuspension of contaminated particles and porewater releases to sediment/water interface, may be important for copper but not for other metals.

Table E-2a. Copper Sediment Monitoring Results by Waterbody (mg/ dry kg)

Waterbody	**Collection dates**	**Org.**	**n**	**Min**	**Max**	**Mean**	**Median**	**% above TEL/PEL**
San Diego Creek	91-99	OCPFRD	172	0.2	53.0	8.5	4.4	4%>TEL
	97-98	IRWD	2	1.0	2.5	--	--	
Upper Bay	91-99	OCPFRD	66	3.0	190.0	23.6	17.0	17%>TEL
	94 & 96	BPTCP	7	5.8	40.80	26.91	35.40	
	00-01	SCCWRP	10	11	58	30.9	25.5	
Lower Bay	91-99	OCPFRD	20	5.0	49.0	25.8	29.5	33%>TEL
	94	BPTCP	11	29.5	240.0	83.7	75.2	
	98	BIGHT	11	10.5	157.4	52.3	39.9	
	99	OGDEN	12	9.5	83	30.8	24	
	00-01	SCCWRP	8	9	130	64.4	63.5	
Porewater	98	BIGHT	9	1.53 ug/L	65.6 ug/L	13.03 ug/L	6.63 ug/L	
Rhine Channel	91-99	OCPFRD	18	29	530	316.5	330	**82%>PEL**
	94 & 96	BPTCP	2	479	505	--	--	
	00	Coastkeeper	2	170	270	--	--	
	00-01	SCCWRP	2	607	634	--	--	

Freshwater Sediment TEL value for Cu is 36 mg/dry kg.
Saltwater Sediment TEL value for Cu is 19 mg/dry /kg; PEL value is 108 mg/dry kg.

Table E-2b. Lead Sediment Monitoring Results by Waterbody (mg/ dry kg)

Waterbody	**Collection dates**	**Org.**	**n**	**Min**	**Max**	**Mean**	**Median**	**% above TEL**
San Diego Creek	91-99	OCPFRD	172	0.8	330	11.3	6.6	6%>TEL
	97-98	IRWD	2	<10	--	--	--	
Upper Bay	91-99	OCPFRD	66	3.3	47	16.8	12.8	5%>TEL
	94 & 96	BPTCP	7	14.2	29.6	20.1	20.4	
	00-01	SCCWRP	10	7	37	18.6	17.5	
Lower Bay	91-99	OCPFRD	20	5.0	36	18.5	18.1	11%>TEL
	94	BPTCP	11	14.8	114	42.6	33.3	
	98	BIGHT	11	7.1	97	37.3	19.8	
	99	OGDEN	12	9.5	51	19.6	13.5	
	00-01	SCCWRP	8	5	30	32.3	22.5	
Porewater	98	BIGHT	9	0.32 ug/L	5.13 ug/L	0.95 ug/L	0.52 ug/L	
Rhine Channel	91-99	OCPFRD	18	26	140	78.5	87.5	54%>TEL
	94 & 96	BPTCP	2	78.1	95	--	--	
	00	Coastkeeper	2	28	58	--	--	
	00-01	SCCWRP	2	72	87	--	--	

Freshwater sediment TEL value for Pb is 35 mg/dry kg.
Saltwater sediment TEL value for Pb is 30 mg/dry /kg; PEL value is 112 mg/dry kg.

Table E-2c. Zinc Sediment Monitoring Results by Waterbody (mg/ dry kg)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median	% above TEL
San Diego Creek	91-99	OCPFRD	173	1.0	200	36.2	22.5	4%>TEL
	97-98	IRWD	2	7.4	12	--	--	
Upper Bay	91-99	OCPFRD	66	4.2	210	79.4	67.2	17%>TEL
	94 & 96	BPTCP	7	46.4	171.0	115.3	136.0	
	00-01	SCCWRP	10	48	169	115	108.5	
Lower Bay	91-99	OCPFRD	20	18.0	130.0	82.3	73.5	37%>TEL
	94	BPTCP	11	86.5	460	219.5	209.0	
	98	BIGHT	11	44.5	260	145	149	
	99	OGDEN	12	30	160	75.5	64	
	00-01	SCCWRP	8	31	248	148	152	
Porewater	98	BIGHT	9	3.85 ug/L	10.9 ug/L	6.06 ug/L	6.11 ug/L	
Rhine Channel	91-99	OCPFRD	18	86	340	198	195	38%>TEL
	94 & 96	BPTCP	2	236	303	--	--	
	00	Coastkeeper	2	77	120	--	--	
	00-01	SCCWRP	2	288	366	--	--	

Freshwater Sediment TEL value for Zn is 123 mg/dry kg.
Saltwater Sediment TEL value for Zn is 124 mg/dry /kg; PEL value is 271 mg/dry kg.

Table E-2d. Cadmium Sediment Monitoring Results by Waterbody (mg/ dry kg)

Waterbody	Collection dates	Org.	n	Min	Max	Mean	Median	% above TEL
San Diego Creek	91-99	OCPFRD	170	0.2	7.4	1.0	0.7	46%>TEL
	97-98	IRWD	2	<0.5	--	--	--	
Upper Bay	91-99	OCPFRD	66	0.2	17.0	2.4	1.4	20%>TEL
	94 & 96	BPTCP	7	0.23	1.17	0.75	0.76	
	00-01	SCCWRP	10	1	2	1.3	1	

Freshwater Sediment TEL value for Cd is 0.6 mg/dry kg.
Saltwater Sediment TEL value for Cd is 0.7 mg/dry /kg; PEL value is 4.2 mg/dry kg

Toxicity

Bay Protection Toxic Cleanup Program
The 1994 State Water Board Bay Protection and Toxic Cleanup Program (BPTCP) results showed Upper Bay, Lower Bay and Rhine Channel sediments were toxic to some forms of aquatic life (two amphipods and fertilization and embryo development of sea urchins). Toxicity was highly significant in both bulk sediments and interstitial porewater at some locations. Direct cause of toxicity was not assessed but statistical correlation was found between toxicity to two amphipod species and sea urchin larvae and elevated levels of numerous chemicals, including copper, lead, and zinc. Benthic organism degradation was also assessed in this study and there was correlation between lower infaunal index and elevated levels of copper (and other organic compounds).

Bight '98
The Southern California Bight Regional Monitoring Project (Bight '98, coordinated by SCCWRP) provides an integrated assessment of Southern California coastal estuaries. Sediments were highly or moderately toxic at 9 of 11 sites in Lower Newport Bay, with no toxicity at two sites close to Newport jetty. Sediment elutriate results yielded toxicity at 7 of 11 sites (Bay et al. 2000). Cause of toxicity was not determined in this study. Benthic degradation was evident at 7 of 11 sites. Correlation of toxicity and chemistry results has also not been completed, in part because some chemistry results are being validated. Nonetheless, bulk sediment metal results (discussed above) indicate elevated levels of copper, lead and zinc at some Lower Bay stations.

Southern California Coastal Water Research Project
Recently, the Southern California Coastal Water Research Project (SCCWRP) has been contracted by Regional Board to complete toxicity identification evaluations (TIEs) of salt waterbodies, including Rhine Channel. Results of this two-year project (still in progress) have consistently detected toxicity (to amphipods and sea urchin larvae) at 8 of 10 sites during September 2000 and May 2001 sampling events (SCCWRP 2001a). Bulk chemistry results are included in these Toxics TMDLs (see Tables E-2 (a -- d) above). Thorough TIE studies in Upper Bay and Rhine Channel are currently in progress and will investigate if metals and / or priority organics are possible causes.

Background

Metals are associated with open-hillside, soils, groundwater, seawater and atmospheric deposition, therefore input of metals via background sources must be evaluated and included in the development of these TMDLs.

Background metals in surface runoff
To date, the best available data for estimating the contribution from runoff of open hillside soils comes from the 319(h) study (Lee and Taylor 2001a). EPA selected dissolved metal results for San Joaquin Channel to provide metal concentrations associated with open spaces. This site was described as 90% open space and 10% agriculture (see Table E-7). No samples were collected during dry weather conditions from this site or any other viable open space site. The range and mean values from this site for two wet weather sampling events are provided in Table E-3. We acknowledge the preliminary nature of these results, yet for lack of other data, we have utilized the mean wet weather values to estimate freshwater (dissolved) loads for medium and high flow tiers.

Table E-3. Metal concentrations in natural soil runoff at San Joaquin Channel

Metal	Range (ug/L)	Mean (ug/L)
Dissolved Cd	0.13 – 0.22	0.17
Dissolved Cu	6.3 – 8.0	7.2
Dissolved Pb	0.097 – 0.13	0.11
Dissolved Zn	7.5 – 16.4	12.0

(source: Lee and Taylor 2001a)

In the summary TMDL document, EPA adjusted OCPFRD estimates of total metals stormwater loads for San Diego Creek and Santa Ana-Delhi Channel using literature values of natural versus anthropogenic contributions. This adjustment was based on information reported by Schiff and Tiefenthaler (2000) who recorded freshwater flows and measured total metals in storm runoff of Santa Ana Watershed, which neighbors the Newport Bay watershed. [This study is the best proxy since no reliable direct measurements of soil runoff within Newport Bay watershed exist to date.] This report provides an assessment of anthropogenic versus natural emissions of metals within surface runoff during the 1998 water year. Using an iron normalization technique, the authors state that Cd, Cu, Pb and Zn were most enriched (33-63%), whereas Cr and Ni were the least enriched (0.5 to 0.7%) due to anthropogenic contributions. Anthropogenic contributions of metals in surface runoff were estimated to be these amounts: 63% (Cd); 42% (Cu); 38% (Pb); 33% (Zn). Percent natural contributions, event mean concentrations (EMC) and median EMCs are summarized in Table E-4.

Table E-4. Total metal results from stormwater monitoring in Santa Ana River Basin in 1998

Metal	Estimate natural (%)	Minimum EMC (ug/L)	Median EMC (ug/L)
Total Cd	37	0.07	0.37
Total Cu	58	7.02	23.3
Total Pb	62	4.07	14.99
Total Zn	67	29.03	93.78

(source: Schiff and Tiefenthaler 2000)

These percent natural contributions have *not* been utilized for developing these dissolved metals TMDLs, since the results were derived from total metals samples.

Groundwater

Remedial Investigation/Feasibility Studies completed at El Toro MACS provide concentration ranges of background contributions of heavy metals in local groundwater. Results range from <2 ug/L for Pb, 4 ug/L for Cd, 21 ug/L for Cu, and 88 ug/L for Zn. Unfortunately these background levels are for unfiltered samples (total metals) collected without using trace metal clean techniques and therefore these results are not reliable for use for these dissolved metals Toxics TMDLs.

Other sources of groundwater data for dissolved metals from shallow (<50 bgs) monitoring wells have yet to be identified within the Newport Bay watershed.

Background metals in ambient seawater

Surface seawater contains metals due to several sources: coastal runoff, ocean upwelling, atmospheric deposition to sea surface, etc. [EPA has designated ambient surface seawater as source of metals but has opted to not differentiate between natural and anthropogenic contributions to surface seawater.] Dissolved metal concentrations in ambient surface seawater are generally quite low (either ppb or less). The range of dissolved metal concentrations in various coastal systems has been reported by Cutter (1991), with more local data supplied from samples collected offshore the Southern California Bight (pers. comm., R. Gossett). Table E-5 that summarizes dissolved metal concentrations in various seawater samples and mean results for Upper Newport Bay water column samples (IRWD 1999) are included for comparison.

Table E-5. Dissolved metal concentrations in saline waters (ug/L)

metal	Calif. Coastal seawater (CRG Lab)	Upper Newport Bay Mean value (IRWD 1999)	Range in Coastal waters (Cutter 1991)
Dissolved Cd	0.1	0.14	0.002 – 0.095
Dissolved Cu	1.4	1.7	0.3 – 3.8
Dissolved Pb	0.1	0.44	0.004 – 0.19
Dissolved Zn	4.1	6.8	0.3 – 30

see text for references

Obviously, inputs of metals from ambient seawater need to be included when determining the background contributions of metals to saline waterbodies of Newport Bay. These inputs are contingent on tidal influences and freshwater flows from San Diego Creek, Santa Ana Delhi Channel and other drainages. During high tides and low freshwater flows, surface seawater contributions would be at their highest levels, whereas during low tides concurrent with storm events would yield much lower contributions from ambient seawater. EPA has used coastal seawater results (CRG Lab) results to approximate inputs from ambient seawater.

III. Source Analysis

OCPFRD estimates

In the 2000 *NPDES Annual Report*, OCPFRD included estimates of total metal stormwater loading from Santa Ana-Delhi Channel, San Diego Creek and two of its tributaries. These estimates are based on monitoring results of unfiltered (composite) water samples and flow measurements at each sampling station collected during wet weather events in each water year. Unfortunately, these total load results do not represent annual loads since not all storm events were samples in the water year. Estimates for 1998 are considered exceptionally high due to El Nino conditions (38.4 inches of rain); whereas 1999 is a slightly dry year (8.8 inches) in comparison to average annual rainfall (13.3 inches) at Tustin/Irvine Ranch site. Table E-6 summarizes these total stormwater load estimates, gives the mean and includes adjustments to display the man-made inputs (Zn = 33.3%, Cu = 41.5%, Pb = 38.3%) as determined by Schiff and Tiefenthaler (2000). No estimates of Cd loading are included in OCPFRD *Annual Report*.

Table E-6. OCPFRD estimates of total metal stormwater loads for San Diego Creek and Santa Ana-Delhi Channel.

Element/ Stn Name	1998 Water year (lbs)	1999 water year (lbs)	2001 water year (lbs)	mean total load (lbs)	Adjusted total load (man-made input) (lbs)
Zn @ PCW	21,575	1306	2964	8615	2869
Zn @ WYL	18,790	1582	3937	8103	2698
Zn @ SDC	63,021	3784	7900	29,908	9957
Zn @ SAD	7031	805	2175	3337	1111
Cu @ PCW	5059	332	862	2084	865
Cu @ WYL	4519	402	956	1959	813
Cu @ SDC	15,087	1643	2020	6250	2594
Cu @ SAD	1643	185	492	770	320
Pb @ PCW	2924	169	356	1150	440
Pb @ WYL	2184	166	407	919	352
Pb @ SDC	10,385	449	1188	12,022	4604
Pb @ SAD	1297	124	369	1790	686

PCW = Peter's Canyon Wash; WYL = San Diego Creek @ Culver;
SDC = San Diego Creek@ Campus; SAD = Santa Ana-Delhi Channel
All results in represent total metals in lbs; for sampled wet weather events only
Adjusted mean = reported mean – % natural calculated from Schiff and Tiefenthaler (2000)

319(h) report

As part of the 319(h) report, Lee and Taylor (2001a) provide estimates of copper loadings based on grab sampling results during two separate storm events in 2000. The authors state that in general the metals data exhibit the highest contributions from "urban stations" and agriculture / open space exhibiting the lowest loadings. They acknowledge the impracticality of making load calculations using grab samples [their methods] as opposed to composite samples [OCPFRD methods], stating "rigorous total load calculations would include the use of constituent concentrations calculated from flow-weighted composite samples taken over the entire runoff hydrograph...Copper loads may be better characterized by OCPFRD NPDES permit stormwater runoff data than the limited single grab sample analysis performed here." Nonetheless, using copper data from Feb. 21, 2000 storm event and corresponding flow data from OCPFRD, the authors estimate metal loadings from specific areas of the watershed. More intriguing are the approximations of total copper loads per acre of tributary drainage area; these provide an estimate of the relative contributions of land uses that are represented at each sampling site. Table E-7 summarizes the dissolved and total copper loads as well as the dominant land use associated with each sampling station.

Table E-7. Land Uses and Total Copper loads for One Storm Event (Feb. 21, 2000)

Sampling station	Dissolved Cu Load (lbs.)	Total Cu load (lbs.)	Total Copper per acre (lbs./acre x 10^{-5})	Dominant land use
San Diego Creek @ Campus	16	159	234	Mixed residential, agricultural, nursery
San Diego Creek @ Harvard	10	169	629	Mixed residential, agricultural, nursery
Peters Canyon Wash @ Barranca	7	39	136	Mixed residential, agricultural, nursery
Hines Channel @ Irvine Blvd	0.2	0.6	94	Nursery, agricultural
San Joaquin Channel @ University	0.2	1.2	136	Agricultural, open space
Santa Ana Delhi	8	28	252	Residential, commercial
El Modena-Irvine Channel	4	8	104	Residential, commercial
Sand Canyon Avenue	N / a	N / a	59	Agricultural
East Costa Mesa @ Highland	N / a		91	Residential, commercial
Central Irvine Channel	N / a	N / a	101	Agricultural, residential, nursery

(Source: Lee and Taylor 2001a)

For the purposes of these *dissolved* metal TMDLs, it is possible to convey dry weather load estimates provided by Lee and Taylor as part of the same 319(h) study (2001a). These dry weather results are based on one filtered grab sample collected during one sampling event and extrapolated use of stream flow volumes (OCPFRD data) recorded during the entire dry season. Table E-8 summarizes the dissolved copper results and for comparison, we include our estimates of dissolved Cu load from the baseflow and small flow tiers as calculated in section IV of this TSD.

Table E-8. Dissolved Copper loads within Newport Bay watershed

Sampling station	**Estimated dry weather Dissolved Cu load* (lbs.)**	**Baseflow and small flow tier Dissolved Cu Load # (lbs.)**
San Diego Creek @ Campus	122.5	1031
San Diego Creek @ Harvard	N/a	--
PetersCynWash @ Barranca	77.65	--
Santa Ana Delhi	238.4	163

*estimated (based on one dry season sample and dry flow records for entire year), source Lee and Taylor 2001a);
#value approximated from chronic targets for base and small flow tiers multiplied by associated flow volumes used in these TMDLs

Metal inputs from Point Sources vs. Non-point sources

Within the Newport Bay watershed, one can reasonably assume the vast majority of metals contributed to fresh and saltwater bodies arise from non-point sources. There are no direct discharges from wastewater treatment plants into San Diego Creek and Newport Bay as is typically true for other waterbodies. There are some discharges of groundwater treatment (cleanup or dewatering) facilities. One study performed in Santa Clara California, identified some of the (non-point) sources of heavy metals from an urban watershed – Lower San Francisco Bay (Woodward-Clyde 1998). Urban road runoff from roads is believed to be the largest contributor of cadmium (tires), copper (brakes and tires), lead (brakes, tires, fuels and oils) and zinc (tires, brakes, auto frame). Secondary contributions come from contaminated sediments, atmospheric deposition and miscellaneous sources, such as antifouling paints from recreational boats. All of these are likely to exist in the Newport Bay watershed.

The possibility remains that individual sites with elevated metal levels may contribute metals to neighboring surface waters, via surface runoff or contaminated groundwater flows. To unveil such contaminated sites EPA has conducted a comprehensive survey of existing databases listing contaminated sites within the Newport Bay watershed. Databases included USEPA National Priority List (NPL), Comprehensive Environment Responsibility, Compensation, and Liability System (CERCLIS), California Department of Toxic Substances Control (DTSC) Calsites and Orange County hazardous material or incidental spill sites (E&I sites). A complete list of sites and associated toxicants is presented in Appendix A. Discussion below narrows the complete survey to information relevant only to metal (Cd, Cu, Pb, Zn) contamination. Information is presented for future exploration/verification of possible metal contaminated runoff from these sites.

Of the Federal sites (NPL and CERCLIS), where preliminary investigations have been completed, only two, Orange Coast Plating and El Toro Military Base, have been shown to have metal contamination. The Orange Coast Plating facility (in Santa Ana) was remediated via soil excavation and surface paving in 1987. It is currently under State regulation and seems unlikely to release trace metals into surface runoff.

Review of RI/FS documents pertaining to El Toro MCAS identified several “hot spots” for heavy metal contamination. Three sites in particular have soil samples with levels in excess (as high as 60x) of background levels. Battery disposal area had high Pb (923 mg/kg dry) and Zn (288 mg/kg dry); Drop Tank Drainage area had high Zn (1760 mg/kg dry) and Cu (548 mg/kg dry) and Materials Management area had high Zn (507 mg/kg dry). No excessive levels of Cd existed in these results. Remediation has either occurred or is planned (pers. comm., M. Smits). To establish if these or other heavy metal hot spots at El Toro are indeed sources one would have to investigate surface runoff during various storm conditions from MCAS base into Marshburn Channel, Borrego Canyon Wash and Agua Chinon Wash. Therefore uncertainty exists if heavy rainfall and subsequent runoff from El Toro sites would transport dissolved and particulate metals into nearby channels, and eventually flow into San Diego Creek.

Tustin Marine Corp Air Station has already remediated metal hotspots (Pb soils); therefore, heavy metal releases into surface runoff and San Diego Creek waterways are believed to be minimal.

Thirty two California DTSC Calsite facilities are located within the watershed, three of which are associated with metal contamination (Appendix A). Two Calsites have very small quantities (Pb soils in planter boxes) and have undergone voluntary cleanups.

Three of twenty four County E&I sites – emergency incidents and industrial clean-ups – were listed for metal contamination; however, these sites (Appendix A) have been remediated or cited that small quantities of surface runoff contamination is likely.

Atmospheric deposition

Deposition of airborne particles may be responsible for contributing specific heavy metals to Newport Bay. Deposition can occur directly as particles settle onto the wet surface or indirectly as they settle on land and are subsequently washed or blown into Upper and Lower Bay. These toxic chemicals are then added to the burden of chemicals in water surface microlayer (a 50 micron boundary layer between atmosphere and water), the water column and/or the sediments. The resultant increase in toxicity may affect aquatic life in Newport Bay. For these TMDLs we have included direct deposition of metal—via both dry and wet processes to surface waters of Upper and Lower Bay, including Rhine Channel. We have not included indirect deposition (fallout or washout to watershed land and subsequent fluvial transport) since it is included in surface runoff concentrations which have already been measured and corrected by background levels.

Average rainfall at Tustin/Irvine weather station is 13 inches per year. EPA used literature cited values from metal deposition studies of San Francisco Bay (Tsai et al. 2001) and Santa Monica Bay (Stolzenbach, et al. 2001). Those studies provide mean dry and wet deposition results for Cu, Pb and Zn. Other studies have included assessments for Cd (Sweet et al. 1997; Golomb et al.1997) which were very small corresponding values so we have disregarded air deposition of Cd for this TMDL. In short this contribution is minimal relative to Cd inputs from other sources, e.g., tributary loading and sediment remobilization.

Saltwater body surface area estimates included mean tidal area of Upper Bay (372.5 acres = 1.5 million sq. meters), Lower Bay (790.2 acres = 3.2 million sq. meters) and Rhine Channel (15.2 acres = 61,000 sq. meters) (GIS data, City of Newport Beach).

Table E-9 Direct Deposition of Metals to surface of Newport Bay

Metal	**Dry Dep (ug/m2/day)**	**Wet Dep (ug/L)**	**Total air dep. (lbs/yr)**
Cd	0.061*	0.4*	3.5
Cu	0.29	2.16	100.7
Pb	0.16	1.47	68.4
Zn	53.57	8.7	606.1

(source: *Tsai et al. 2001; all other values from Stoltzenbach et al. 2001)

Recreational Boats (for Cu)

EPA has utilized information from San Diego RWQCB Dissolved Copper TMDL (for Shelter Island Yacht Basin) to estimate copper inputs from recreational boats to Newport Bay. The San Diego TMDL, currently in draft status, provides dissolved copper loading equations for both passive leaching from wetted hull surfaces and from underwater hull cleaning (i.e., wiping down the wetted surface to remove marine growth). Briefly, EPA has applied local conditions (number of moored boats) for Newport Bay, assumed similar mean boat length and wetted surface area and used equations from the San Diego TMDL to give preliminary estimates of dissolved copper loads per year. Passive leaching contributes approximately 35,000g / day (77 lbs / day) and hull cleaning about 27,279 g / day (60 lbs / day). More explicit details for these calculations are provided in Section IV of this TSD.

Summary of Monitoring results and Source analysis

- In freshwater bodies, water column measurements of dissolved metals exceed water quality standards during wet weather events. Sediment metal concentrations rarely exceed TEL values in freshwater bodies, except for Cadmium. Sediment metal levels generally increase along the freshwater to saltwater gradient, with maximum levels found in Rhine Channel. Porewater results indicate fluxes of dissolved copper may occur at levels of concern within Lower Bay, but this is unlikely for other metals. Transport of metals from fresh to saline systems may contribute to toxicity problems observed in Newport Bay sediments.
- OCPFRD loading estimates, uncorrected for anthropogenic inputs and based on unfiltered composite samples collected during storm events, demonstrate direct relationship with flow conditions; i.e., heavy storm years yield high metal loads in surface runoff. Inputs from San Diego Creek (90%) far outweigh those from Santa Ana-Delhi Channel (10%). For two tributaries of San Diego Creek, Peters Canyon Wash (54%) contributes slightly more heavy metals than those from waters upstream of San Diego Creek at Culver (46%).
- Lee and Taylor (2001a) estimates of metal loading are generally lower than OCPFRD's, however there are differences in sampling techniques and collection approach (grabs versus composites). Dissolved metal levels are much lower than those measured in total (unfiltered) metals samples. It is difficult to utilize the 319(h) results to approximate stormwater loads of dissolved metals due to lack of adequate monitoring during peak flows (Lee and Taylor 2001a). Nonetheless, dramatic decreases in metal concentrations during all weather conditions may occur if trace metal clean sampling methods are utilized by all those sampling for metals in surface or groundwaters with Newport Bay and the surrounding watershed.
- Assessment has included ambient surface seawater results as well as approximate open space runoff contributions. Based on unfiltered samples, total metal results may be adjusted to demonstrate anthropogenic contributions, Zn = 33%, Pb = 38%, Cu = 42%, Cd = 63% (Schiff and Tiefenthaler 2000). To date, no useful groundwater results exist within the San Diego Creek watershed. Air deposition and ambient seawater sources are deemed to be minor sources to Newport Bay.
- Using TMDL studies nearly completed in San Diego Bay, recreational boat hulls may be the single largest contributor of dissolved copper in saltwater bodies of Newport Bay. Our extrapolation of methods presented in the San Diego yacht harbor for passive leaching and underwater hull cleaning suggest as much as 80% of all copper inputs to Newport Bay. These preliminary results suggest that dissolved copper from boat hulls is a significant non-point source in Lower Bay and may be carried into Upper Bay with tidal flows.

Table E-10. Summary of (estimated) metal inputs to San Diego Creek (lbs/yr)

	Cd	Cu	Pb	Zn	
Stormwater[1]	N/a	6250	12,022	29,908	
Groundwater[2]	Unknown	Unknown	Unknown	Unknown	
Nurseries/ Other ag. [3]		214		4	
Open space runoff[4]	221	622	335	12,392	
Total	>221	>7086	>12,357	>42,304	

[1] total metal loads from stormwater samples -- not adjusted (OCPFRD 2000)

[2] inputs from groundwater could be significant although reliable monitoring data from numerous sites in the watershed are required for assessment

[3] value is approximation of total metals applied to all agriculture crops in watershed, equivalent to twice the value of total metals applied by three nurseries in 1996 (Lee and Taylor 2001b)

[4] dissolved metals, based on San Joaquin Channel mean concentration reported in 319 (h) study (Lee and Taylor 2001a) multiplied by medium and large flow tier volumes.

Table E-11. Summary of Total metal inputs to Newport Bay (lbs/yr)

	Cd	Cu	Pb	Zn	
freshwater[1]	N/a	7020	13,812	33,245	
Recreational Boats [2]	negligible	50,114	negligible	Unknown	
Air deposition[3]	3.5	101	68.4	606	
Ambient seawater[4]	389	777	233	9330	
Porewater[5]	negligible	Unknown	negligible	negligible	
Total	393	58,002	14,113	43,181	

[1] sum of total metal loads from stormwater samples collected in 2000 from San Diego Creek and Santa Ana-Delhi (OCPFRD)

[2] preliminary estimate of dissolved copper from passive leaching and hull cleaning (see TSD section IV)

[3] estimate for direct deposition of metal to surface waters of Newport Bay only (see TSD section IV)

[4] estimate of dissolved metal inputs from ocean based on local data (pers. comm. R. Gossett) and approximate ocean volume into Newport Bay (see section IV on Newport Bay "bathtub model")

[5] porewater results from Bight '98 study (SCCWRP in prep)

IV. *Approach to calculating mass-based Loading Capacity*

Freshwater loads of dissolved metals
In the DRAFT summary TMDL document, EPA selected to use the flow based approach to determine mass based dissolved metal loads in freshwater bodies. In this approach, the continuous range of river flow that occurs at each target site is broken down into ranges or tiers. Target dissolved metal concentration multiplied by volume associated with each tier gives the dissolved metal load per flow tier; the sum equals the loading capacity. The applicable allocation for a given source does not depend on the time of year, rather on the actual creek flow at the time of discharge and associated hardness value. So flow rate determines hardness which in turn dictates the appropriate metals criteria or target. Complete discussion of freshwater flows in San Diego Creek and Santa Ana Delhi are presented in TSD Part B – Flow.

Here is an explanation of the sequence of steps to determine metals criteria associated with each flow tier. We use small flow tier and dissolved copper target as an example.

1. Range of flow is 21 to 181 cfs. Choose highest flow rate within the tier = 181 cfs.
2. Use linear equation to find corresponding hardness value….start with natural log (flow rate)
3. For San Diego DCreek, hardness = -57.742 (ln [flow])+ 622.5
4. Use this hardness value (322 mg/L as $CaCO_3$) in CTR equations to determine acute and chronic criteria for each metal.
5. Dissolved chronic Copper criteria = e(0.8545[ln(hardness)]-1.702)*0.96 =24.3 ug/L

Table E-12. Calculation of dissolved metal loading capacity for San Diego Creek (at Campus)

Copper	**Range of Flow rates**	**Hardness applied**	**Flow volume**	**Target metal conc.**	**loading per tier**	**% total**
	(Q)	(mg/L)	(ft3)	(mg/L)	**(lbs)**	
baseflow	Q <20	400	275,411,823	0.0293	503.78	23%
Small flow	20<Q<181	322	347,504,437	0.0243	527.18	24%
Medium flow	181<Q<814	236	357,632,336	0.0187	417.51	19%
Large flow	Q > 815	197	468,824,589	0.0255	746.35	34%
			1449,373,185 Total volume		2194.83 **lbs/yr**	

Flow volume per tier is based on 19 water year average: 1977/78, 1984/85 to 2000/01
Target metal concentration is hardness dependent.

This methodology was utilized for calculating dissolved metal load estimates from Santa Ana-Delhi Channel too. Chronic conditions applied to base, small and medium flows, acute conditions applied to large flows. Daily flow records for Santa Ana-Delhi Channel covered six water years: 1995/96 – 2000/01. Using method outlined in Table E-12, dissolved copper inputs from Santa Ana-Delhi Channel would be approximately 303 lbs/yr. Thus total freshwater inputs from SAD and SDC would be less than 2499 lbs/yr. This is a conservative estimate based on chronic concentrations for much of the year, whereas higher concentrations may exist and be tolerated by freshwater organisms during short term (acute) exposures.

Dissolved metal loads in Newport Bay via "bathtub model"

The following information and equations were used to evaluate loading capacities in Newport Bay. We did not differentiate between Upper & Lower Bay & Rhine Channel since these water bodies are inherently intertwined when considering dissolved constituents. As you can see this "bathtub model" incorporates data for dissolved and total metal concentrations, freshwater flows, ebb and flood tides, and the volume of the Bay

The mass balance of water and pollutant can be written as follows:

$$\frac{dV}{dt} = (Q_0 - Q_b + Q_f)$$

$$\frac{dVC}{dt} = Q_0 C_0 - Q_b C + L_f + L_l - Av_s F_d C_T$$

where

C = dissolved pollutant concentration (mg/L)
C_T = total pollutant concentration (mg/L)
Qf = freshwater inflow
Q_0 = the quantity of water that enters the bay on the flood tide through the ocean boundary that did not flow out of the bay on the previous ebb tide (m^3/T)
Q_b = the quantity of water leaving the bay on the ebb tide that did not enter the bay on the previous flood tide (m^3/T)
V = volume of the bay
T = period of dominant tidal period (day)
L_f = loading from upstream (g/day)
L_l = loading from local area (additional sources within the bay; e.g., boats) (g/day)
A = surface area of the bay
v_s =net settling velocity (m/day)
F_p = fraction of particulate pollutant

At steady state

$$Q_b = Q_0 + Q_f$$

$$Q_b C + Av_s F_p C_T = Q_0 C_0 + L_f + L_l$$

The volume of new ocean water entering the bay on the flood tide can be determined by using ocean tidal exchange ratio (R_0) as

$$Q_0 = R_0 Q_T$$

where R_0 = exchange ratio and Q_T = total volume of ocean water entering the bay on the flood tide. The exchange ratio can be estimated from salinity data (Fischer et al. 1979)

$$R_0 = \frac{S_f - S_e}{S_0 - S_e}$$

Where S_f = average salinity of ocean water entering the bay; S_e =average salinity of bay water leaving the bay; and S_0 = Salinity at ocean side. The volume of mixed bay water Q_b leaving the bay on the ebb tide can be determined by using tidal exchange ratio (R_b)

$$R_b = \frac{S_f - S_e}{S_f - S_b}$$

where S_b is salinity of mixed bay water.

The flushing time (residence time) T_L can be calculated as follows:

$$T_L = \frac{V_b}{Q_b}$$

Where V_b = mean volume of the bay (19 million m^3 from RMA 2001). The exchange ratio R_0 can be estimated from the salinity observation data (RMA 1999). The ratio varies from 0.20 to 0.30. It can also be estimated through model calibration. The ratio used in the model is 0.25. Use median freshwater input of 16cfs, Q_b can be estimated.

Assume 0.80 as dissolved fraction of copper. ($C+0.2\ C_T = C_T$, $C_T = 1/0.8C$.)
Therefore, $C_T = 1.25\ C$ and the pollutant concentration in the bay can calculated as follows:

$$C = \frac{Q_0 C_0 + L_f + L_l}{Q_b + 1.25 A v_s F_p}$$

Let C_c be the criteria of Cu in the Bay, the loading capacity can be estimated as

$$Load = C_c (Q_b + 1.25 A v_s F_p) - Q_0 C_0$$

The results are listed in Table E-13.

Table E-13 “Bathtub” Model Results for dissolved copper

Bay volume (m^3)	Con. at ocean side (ug/L)	Exchange ratio	Volume entering Bay_0 (m^3/day)	Freshwater Cu Loading (lbs/yr)*	Estimated concentration (ug/L)	Criteria (ug/L)	Loading capacity (lbs/yr)
19000000	1.4	0.25	4,830,918	2499	3.03	3.1	11646

* This estimate assumes substantial reductions (>five fold) in copper loading from hull leaching and boat maintenance.

Calculations of direst atmospheric deposition load to Newport Bay

For these TMDLs, atmospheric concentrations reported in scientific literature were utilized for each metal to estimate the overall mass deposition into the Bay, F. There are two types of direct deposition: dry and wet. Dry deposition involve the transport and surface accumulation of particulate air contaminants during periods without precipitation. Wet deposition involves the removal of pollutant from the atmosphere via various precipitation processes ("washout"). Both dry and wet deposition are considered in this general equation.

$$F = C * V * S$$

Where

C = ambient air concentration (ug / m^2 / day or ug / L)
V = deposition velocity (m / yr)
S = total surface area for deposition (m^2)

Table E-14. Direct Air Deposition of metals to Newport Bay surface waters

	dry (ug / m2 / day)	wet (ug / L)	total dry (g / yr)	total wet (g / yr)	total air load (g / yr)	total air load (lbs / yr)
Cd	0.061	0.11	3.34E+01	1574.85	1.61E+03	3.5
Cu	0.29	2.16	5.04E+02	45153.29	4.57E+04	100.7
Pb	0.16	1.47	2.78E+02	30729.32	3.10E+04	68.4
Zn	53.57	8.7	9.31E+04	181867.42	2.75E+05	606.1

Pesticide Use Reports

Pesticide Use Reports for three nurseries (Bordier's, El Modeno, and Hines) show relatively small amounts of copper (about 20, 15, and 72 lbs. respectively) per year and even smaller amounts of zinc (2 lbs. or less). (source: Lee and Taylor 2001b)

Methods to estimate Cu loads from boat hulls

EPA has utilized information compiled by San Diego RWQCB as part of the Dissolved Copper TMDL for Shelter Island Yacht Basin (SD RWQCB 2001 and references therein). The Shelter Island TMDL is nearly complete and has relatively robust data to support their estimates of leaching off boat hulls. Typically owners rely on copper-based antifouling paints to minimize algae growth on boat hulls, thus both passive leaching and underwater hull cleaning result in release of dissolved copper into Newport Bay. Common maintenance practices involve underwater hull cleaning about once per month, with much less frequent removal for dry-dock repainting. [Above water hull cleaning or dry-docking occurs within boatyards and discharges containing copper from antifouling paints are regulated by diversion into pre-treatment systems and then sewer drains or into local sumps.]

EPA has assumed that similar boat maintenance practices occur in Newport Bay harbors. Further we use the same assumptions about mean boat length and wetted surface area as presented in the Shelter Island Yacht Basin Dissolved Copper TMDL. One difference is applied--approximately 10,000 boats are moored in Newport Harbor (pers. comm., T. Melum). We recognize this extrapolation of methods and values from one location to another may not be construed as exact science; however, it does serve as first approximation until further site specific data has been accomplished.

The Shelter Island Dissolved Copper Draft TMDL includes information from boat studies performed in 1994 and 1995. Additional studies are currently in progress to refine these preliminary studies and establish more substantial data sets for hull cleaning and passive leaching. Results from these additional studies were not available for these Newport Bay Toxics TMDLs. References included below are from the Shelter Island Dissolved Copper TMDL. Adjustments for *data applicable to Newport Bay are in italics.*

Passive Leaching

In San Diego Bay, the majority of recreational vessels are sailboats that range in length from 30 to 40 feet (9.1 to 12.2 meters) (Conway and Locke 1994, Southwestern Yacht Club 2000). In the SIYB, the average size recreational vessel is 40 feet in length (12.2 meters), with a beam width of 11 feet (3.4 meters) (Bay Club 2000, Half Moon Marina 2000, Southwestern Yacht Club 2000, Conway and Locke 1994). Average wetted hull surface area is calculated based on this average size vessel, which is then used to calculate the amount of passive leaching over time per vessel. Wetted hull surface area is calculated using the following equation: Wetted hull surface area = (Overall length)*(Beam height)*(0.85) (Interlux 1999).

Dissolved copper loading from all of the recreational vessels in the SIYB is calculated from the average number of vessels known to reside there. Copper loading from passive leaching is calculated as follows:

Annual copper load (kg/yr.) = P*S*N, and S = L*B*0.85

Where:
P = Passive leaching rate
N = Number of boats
S = Wetted hull surface area = Overall length*Beam*0.85
L = Average length
B = Average beam height
Given:
P = 10 $\mu g/cm^2/day$
N = 10,000 (number of boats moored in Newport Bay)
L = 12.2 m (= 40 ft)
B = 3.4 m
Wetted hull surface area = (Overall length)*(Beam height)*(0.85)
Wetted hull surface area = (12.2 m)*(3.4 m)*(0.85) = 35.3 m^2
Annual load = (10 $\mu g/cm^2/day$)*(35 m^2)*(*10,000* vessels)*(10,000 cm^2/m^2)*(kg/10^9 μg)(365 day/yr.)

Estimates of Copper load from passive leaching in Newport Bay= 12,775 kg/year (35,000 g/day).

Hull Cleaning

Underwater hull cleaning (hull cleaning) is a common maintenance practice designed to prevent buildup of marine organisms on a ship's hull. Although antifouling paints are effective at halting growth, some growth does occur which will build up over time. This growth may be removed from recreational vessel hulls either through haul-out at a boatyard, or manually while the boat is in-water using underwater hull cleaning techniques (SCCWRP 2000). It has been estimated that almost all of the pleasure crafts in the Shelter Island Yacht Harbor undergo periodic underwater hull cleaning (SCCWRP 2000).

The physical process of removing marine growth on a ship's hull underwater results in a release of dissolved copper from the paints. The amount of copper released from hull cleaning is dependent on cleaning frequency, method of cleaning, type of paint, and frequency of painting. It was been estimated that underwater hull cleaning takes place in San Diego Bay about ten times a year for regularly maintained recreational boats (Conway and Locke 1994). (*this rate is also assumed to apply to boats in Newport Bay)* In addition, it was determined that painting frequency varies from one to three years, with most vessels being repainted every two years (Johnson et al 1998, Conway and Locke 1994). However, there are no known published studies that quantitatively compare release rates based on paint age, paint type, or method of cleaning. It is reasonable to assume that those frequently painted vessels with higher copper content paints will release more copper during hull cleanings. It is also reasonable to assume that more abrasive cleaning techniques tend to release more copper. However, published studies that provide quantitative estimates of copper loading from underwater hull cleaning are limited, particularly for recreational vessels.

Prior to the hull cleaning, dissolved copper concentrations in the vicinity of the boat averaged 12 µg/L. During the hull cleaning, average concentrations increased from 12 µg/L to 56 µg/L. Concentration levels decreased to 17 µg/L within five minutes after the cleaning ended, and levels returned to background within ten minutes. Researchers found that the copper contaminant plume moved with the current, and that the degree of plume contamination was dependent upon fouling extent and exertion by the diver (McPherson and Peters 1995). Based on the results, the authors concluded that underwater hull cleaning generates elevated concentrations in the vicinity of the operation, which return to background levels in a short time (within minutes).

More studies are needed to fully evaluate the environmental impacts of underwater hull cleaning over a range of environmental conditions and cleaning techniques. The Southern California Coastal Water Research Project Authority (SCCWRP), in collaboration with the Regional Board, is currently investigating environmental effects of antifouling paints and underwater hull cleaning activities in San Diego Bay as part of a two-year research grant. Funding for this research was provided by the State Water Resources Control Board (SWRCB) through the USEPA 319(h) Nonpoint Source Implementation Grant Program. Results from this study should provide greater information about the environmental impacts from underwater hull cleaning.

<u>Calculations</u>

Copper loading from hull cleaning was calculated from information provided in the studies by PRC (1997) and McPherson and Peters (1995). In the McPherson and Peters study, an underwater hull-cleaning event was monitored for dissolved copper concentrations in the resulting plume. Plume concentrations ranged from 40 µg/L to 83 µg/L, with a mean of 56 µg/L. Prior to the hull-cleaning event, concentrations in the SIYB averaged 12 µg/L (McPherson and Peters 1995). Equations for the determination of plume and copper concentration in the plume were provided by PRC (1997).

Plume concentration (P_c) = (Total plume concentration) – (Background concentration)

$$P_c = (56\ \mu g/L) - (12\ \mu g/L) = 44\ \mu g/L$$

Plume volume (P_v) = L_p*W_p*D_p
P_v = (L_b + 6 m + 6 m)*(W_b + 6 m + 6 m)*(6 m)
P_v = (24.2 m)*(15.4 m)*(6 m) = 2236 m^3 per cleaning event

Where:
P_c = Plume concentration
P_v = Plume volume
L_p = Average plume length
W_p = Average plume width
D_p = Average plume depth
L_b = Average boat length
W_b = Average boat width
D_p = Average plume depth

Given:
L_b = 12.2 m
W_b = 3.4 m

Annual copper load = N_h*P_v*P_c*N_v
= (10 / yr.)*(2236 m^3)*(44 µg / L)*(*10,000* vessels)*(kg / 10^9 µg)*(1000 L / m^3)

Where:
N_h= Number of hull cleaning events / year
P_v = Plume volume
P_c = Plume concentration
N_v = Number vessels

Given:
N_h = 10 / year
P_v = 2236 m^3
P_c = 44 µg / L
N_v =10,000 estimated occupancy

Estimates of Copper load from hull cleaning in Newport Bay = 9838 kg / year (27,279 g / day)

New Cd criteria:
EPA has recently issued a revised ambient water quality criteria for dissolved cadmium (EPA 2001a). While the State of California has yet to adopt this criteria, it is useful to provide the equations to determine the freshwater dissolved criteria as well as the corresponding revised concentration based allocations for San Diego Creek.

Dissolved acute Cadmium criteria = $e^{*}(1.0166[\ln(\text{hardness})]-3.924)*0.908$

Dissolved chronic Cadmium criteria = $e^{*}(.7409[\ln(\text{hardness})]-4.719)*0.873$

Table E-15. Current dissolved Cd Numeric Targets (ug/L) based on flow tiers for San Diego Creek.

Dissolved Metal	Base Flows (<20 cfs) hardness @ 400 mg/L		Small Flows (21 - 181 cfs) hardness @ 322 mg/L		Medium Flows (182 -815 cfs) hardness @ 236 mg/L		Large Flows (>815 cfs) @ 197 mg/L
	Acute	Chronic	Acute	Chronic	Acute	Chronic	Acute
Current Cd	19.1	6.2	15.1	5.3	10.8	4.2	8.9
Proposed Cd	7.7	0.64	6.3	0.55	4.6	0.45	3.9

Proposed Cd targets based on recently revised ambient water quality criteria (EPA 2001a)

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Appendix A: DTSC Calsite facilities within Newport Bay watershed

Site ID number	Facility Name	Address	City	Chemicals of concern	Comment
30970007	Tustin Parcel	Corner of Edinger Ave. And Harvard Ave.	Tustin	Pesticides near housing project; Elevated As in shallow soil samples	Nfa for pesticides (1994); As area under investigation (2001)
Same (?)	Tustin Parcel	Corner of Barranca Pkwy and Harvard Ave.	Tustin		Maybe same site as above
30970004	Costa Mesa Air National Guard	South of Presidio Dr.	Costa Mesa	Waste fuel, paint, oil, solvents	Active site; Sampling plan submitted 6/01
30970002	Tustin Marine Corps Air Station	Edinger Avenue	Tustin	Numerous chemicals have been remediated, MTBE plume, As soil	DTSC active site
30790003	Orange County International Raceway	15000 Sand Canyon Avenue	Irvine	Waste oils	Converted to commercial sites (1991) Nfa by DTSC (1994)
30750008	G & H Radiator Service	120 S. Main Street	Santa Ana	Auto radiator waste	Nfa by DTSC (1994)
30510001	Avalon Chemical Company Incorporated	1230 Saint Gertrude Place	Santa Ana	Solvents, acids, bases	Referred to RCRA (1995)
30490110	Edison/Santa Ana II	N.W. of 2nd St. and Sycamore St.	Santa Ana	PAHs, VOCs, heavy metals	DTSC approved RI/FS in 2001, vol. cleanup
30490108	Southern California Gas/Santa Ana I	Corner of Minnie St. and E. Walnut	Irvine	PAHs and Pb	Preliminary endangerment assess. in 1997, still DTSC site
30490008	Coyote Canyon Sanitary	South of Bonita	Irvine	On-site disposal	Referred to County and RWQCB (1989)

Site ID number	Facility Name	Address	City	Chemicals of concern	Comment
	Landfill	Canyon on Coyote Canyon			
30370015	Ford Aerospace Corporation	1000 Ford Road	Newport Beach	Haz. Material handlers, TSD facility	Referred to RCRA (1995)
30360252	Universal Circuits	1800 Newport Circle	Santa Ana	VOCs, heavy metals in soil	Referred to County (1995)
30360188	Engineered Electronics Company	1441 E. Chestnut	Santa Ana	TSD large facility generator	Nfa by DTSC (1996)
30360052	Hughes, Connecting Devices Division	17150 Van Karman	Irvine	(Poor drum storage)	Nfa by DTSC (1982); Referred to RCRA (1995)
30360008	Metropolitan Circuits Inc.	1261 Logan Avenue	Costa Mesa	Cu and metals in soil	Soil remediation in 1995, Nfa by DTSC
30350177	B & D Metal Finishing	1901 Westminister Avenue	Garden Grove	Solvents	Referred to County (1984)
30350014	Audio Magnetics	2602 Michelson	Irvine	VOCspill (1976)	Nfa by DTSC (1984)
30340301	Rheem Metals	1722 S. Santa Fe Street	Santa Ana	Uncertain	Soil removed 1982, certified clean by DTSC (1982)
30340300	Circuit One	2101 Grand Ave.	Santa Ana	Pb, sludge waste, acids, bases	PEA complete (1984); Nfa by DTSC (1994)
30340067	Smith Tool Company	17871 Von Karman	Irvine	Waste oil and metals	Referred toRWQCB (1995); Nfa by EPA and DTSC
30340061	Rockford Aerospace Products	17300 Redhill	Irvine	Waste oil, cyanides, acids, solvents	Referred to County (1991)
30340054	Orange Coast Plating	2515 S. Birch St.	Santa Ana	Metal sludge, acids, cyanide	Site inspection approved by EPA (1997); Nfa by

Site ID number	Facility Name	Address	City	Chemicals of concern	Comment
					RWQCB (1999)
30340013	Embee Plating	2144 South Hathaway	Santa Ana	VOCs, metals, solvents, acids	Referred to RWQCB (1995)
30330070	Aluminum Forge	502 E. Alton	Santa Ana	Waste oil and mixed oil	Referred to County after EPA and DTSC deem Nfa (1991)
30300129	Newport Adhesives Composites	1822 Reynolds Avenue	Irvine	TCE, PCE, TPHs,	PA completed (1996), no action since
30280534	Extruded Plastics Company	2201 S. Standard	Santa Ana	Unspecified liquids	Referred to RWQCB (1982)
30280530	Exotic Material, Inc.	2930 Bristol St.	Costa Mesa	Wate oil, solvents, acids	Nfa (1994)
30280469	Holchem DBA Service Chemical	1341 E. Maywood St.	Santa Ana	Uncertain	Site is residential area (1982)
30280370	Zeus Manufacturing	2970 Airway Avenue	Costa Mesa	Solvents, metals, acids	PA done by EPA (1988) Nfa by DTSC (1995)
30280149	McKesson Chemical	1302 Industrial Drive	Tustin	Pseticides and solvents in drums	Nfa by DTSC (1994); referred to County
30280073	Tibbetts Newport Company	2337 Birch St.	Santa Ana	Pesticide containers, paint sludge	Referred to County (1987)
30280006	Consolidated Thermoplastics	2520 S. Birch St.	Santa Ana	Pb, Cr, waste oil, solvents	Nfa by EPA (1989); Nfa by DTSC (1989)

Nfa = no further action; PEA = preliminary endangerment assessment
DTSC contact, Carole Mah, (916) 323-3397

Appendix A (cont.): Orange County Health Care Agency comments on DTSC Calsites.

SITE NUMBER	SITE NAME	OCHCA INFORMATION
30970007	Tustin parcel	No information
30970004	National Guard	Clean up closed 6-93, clean operation
30970002	MCAS	DTSC clean up no HCA involvement
30790003	O C Raceway	No info, not a current site
30750008	G&H Radiator	No info, not a current site
30510001	Avalon chemical	No info, not a current site
30490110	Edison	No info, not a current site
30490108	SC Gas	No info, not a current site
30490008	Coyote landfill	Landfill closed 1991, regular LEA monitoring
303700015	Ford Aerospace	Facility closed 1998
30360252	Engineered Electronic	No info, not a current site
30360052	Hughes	Clean operation
30360008	Metro Circuits	Velie Circuits, clean site
30350177	B&D metal	No info, not a current site
30350014	Audio magnetics	No info,not a current site
30340301	Rheem Metals	No info, not a current site
30340300	Circuit One	Active clean up, no problems
30340067	Smith Tool	Clean up closed 4-86
30340061	Rockford Products	No info, not a current site
30340054	Orange Coast Plate	Clean up referred to DTSC 11-95
30340013	Embee Plating	Clean up referred to DTSC 5-96, clean opera
30330070	Aluminum Forge	Clean up closed 10-87
30300129	Newport Composites	Clean facility
30280534	Extruded Plastics	No info, not current site
30280530	Exotic Material	No info, not current site
30280469	Holchem	No info, not current site
30280370	Zeus	Chart Industries, clean site
30280149	McKesson	No info, not current site
30280073	Tibbetts Newport	No info, not current site
30280006	Consolidated Therm	No info, not current site