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STATION	DATE/TIME	SAMPLES	Turb	EC	pH	NO3	NH3	TKN	PO4	oP	TSS	VSS	Cd	Cr	Cu	Pb	Ni	Âg	Zn	Hardness
· · · · ·		Type #	NTU	umhos		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	μg/L	μ g/L	μ g/L	μ g/L	μ g/L	μg/L	μg/L	mg/L
								E	ast Basir	٦.										
DAPTEB	11/21/00 0:00	D	2.7	54100	7.9	<0.44	0.059	1.1	<0.061		20	<10				-				
DAPTEB	1/24/01 0:00	ST	4.6	48400	7.9	0.65	0.054	0.68	<0.061		25	<10	ʻ <1	<8	3.5	<2	14	<2	31	
DAPTEB	1/24/01 0:00	SF											<1	<8	<2	<2	15	<2	27	
DAPTEB	1/26/01 0:00	ST	5.6	44200	8	0.49	<0.05	0.47	<0.061		34	<10	<1	<8	<2	<2	20	<2	12	
DAPTEB	1/26/01 0:00	SF											<1	<8	<2 <2	<2	28	<2	<10	
DAPTEB	1/28/01 0:00	ST	2.3	54500	8.1	<0.44	<0.05	0.43	<0.061		36	<10	<1	<8>	8.7	<2	25	<2	33	
DAPTEB	1/28/01 0:00	SF											<1	<8	3.2	<2	24	<2	24	
DAPTEB	2/26/01 0:00	ST	23	33420	7.7	1.2	0.064	0.47	0.459		14	<10	<1	<8	8.1	<2	16	<2	29	
DAPTEB	2/26/01 0:00	SF 🕤											<1	<8	<2	<2	16	<2	15	
DAPTEB	2/28/01 0:00	ST	6	41900	8	0.88	<0.05	0.52	0.184		26	<10	<1	<8	<2	<2	35	<2	17	
DAPTEB	2/28/01 0:00	SF											<1	<8	<2	·<2	48	<2	83	
DAPTEB	3/2/01 0:00	ST	2.1	45900	8	<0.44	<0.05	0.39	<0.061		12	<10	<1	<8	<2	<2	49	<2	20	
DAPTEB	3/2/01 0:00	SF											<1	9.4	<2	<2	42	<2	39	
DAPTEB	6/28/01 0:00	D	3.5	44190	8	<0.44	<0.05	0.84	0.122		11	<10						•		

Appendix L-3

STATION	DATE/TIME	SAMPLES	Turb	EC	pН	NO3	NH3	TKN	PO4	oP	TSS	VSS	Cd	Cr	Cu	Pb	Ni	Ag	Zn	Hardness
		Type #	NTU	umhos		mg/L_	_mg/L_	mg/L	mg/L	_mg/L	mg/L	mg/L	μ g/L	μg/L	μ g/L	mg/L				
								Harb	or Entra	nce					•					
DAPTHE	1/24/01 0:00	ST	2.9	53200	8	<0.44	<0.05	0.637	<0.061		12	<10	<1	.<8	<2	<2	17	<2	19	
DAPTHE	1/24/01 0:00	SF			•								<1	<8	<2	<2	19	<2	17	
DAPTHE	1/26/01 0:00	ST	2.8	49800	8	<0.44	<0.05	0.38	<0.061		25	<10	<1	<8	7.3	<2	- 23	<2	36	
DAPTHE	1/26/01 0:00	SF											<1	<8	2	<2	- 24	<2	23	
DAPTHE	1/28/01 0:00	ST	76	55700	8.1	<0.44	<0.05	<0.2	<0.061		250	13	<1	<8	<2	<2	32	<2	<10	
DAPTHE	1/28/01 0:00	SF											<1	<8	<2	<2	56	<2	<10	
DAPTHE	2/26/01 0:00	ST	50	28060	8.1	1.9	0.077	0.46	0.643		66	<10	<1	<8	<2	<2	16	<2	13	
DAPTHE	2/26/01 0:00	SF											<1	<8>	<2	· <2	16	<2	<10	
DAPTHE	2/28/01 0:00	ST	21	42270	8	0.88	<0.05	0.55	0.214		47	<10	<1	<8	<2	<2	35	<2	12	
DAPTHE	2/28/01 0:00	SF											<1	<8	<2	<2		<2	<10	
DAPTHE	3/2/01 0:00	ST	4.1	46300	8.1	<0.44	<0.05	. 0.4	<0.061		10	<10	<1	9.4	<2	<2	36	<2	<10	
DAPTHE	3/2/01 0:00	SF									-		<1	9.4	<2	<2	35	<2	<10	

Appendix L-4

STATION	DATE/TIME	SAMPLES	Turb	EC	pН	NO3	NH3	TKN	PO4	oP	TSS	VSS	Cd	Cr	Cu	Pb	Ni	Ag	Zn	Hardness
		Туре #	NTU	umhos		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	μ g/L	μ g/L	μ g/L	μg/L	μ g/L	μg/L	μg/L	mg/L
<u></u>								Lau	inch Ran	np			•							
DAPTLB	11/21/00 0:00	D	1	54900	8.1	<0.44	0.07	0.9	<0.061		20	<10								
DAPTLB	1/24/01 0:00	ST	3.5	50500	. 8	<0.44	<0.05	0.57	<0.061		33	<10	<1	<8	<2	. <2	16	<2	18	
DAPTLB	1/24/01 0:00	SF											<1	<8	<2	<2	16	<2	15	
DAPTLB	1/26/01 0:00	ST	5.3	47300	8	0.44	<0.05	0.42	<0.061		18	<10	<1	<8	2.4	<2	20	<2	65	
DAPTLB	1/26/01 0:00	SF											<1	<8	<2	<2	21	<2	17	
DAPTLB	1/28/01 0:00	ST	2.7	54300	8	<0.44	<0.05	<0.2	<0.061		. 18	<10	<1	<8	8.8	<2	23	<2	26	
DAPTLB	1/28/01 0:00	SF				•							<1	<8	<2	<2	26	<2	14	
DAPTLB	2/26/01 0:00	ST	8.9	36600	8.1	0.65	<0.05	0.3	0.184		29	<10	<1	<8	<2	<2	16	<2	24	
DAPTLB	2/26/01 0:00	SF											<1	<8	<2	<2	16	<2	15	
DAPTLB	2/28/01 0:00	ST	5.4	44520	8	0.44	<0.05	0.52	0.0918		29	. <10	<1	8.4	<2	<2	40	· <2	11	
DAPTLB	2/28/01 0:00	SF											<1	9.4	<2	<2	42	<2	12	
DAPTLB	3/2/01 0:00	ST	2.5	46300	8.1	<0.44	<0.05	0.45	<0.061		33	<10	<1	<8	<2	<2	27	<2	<10	
DAPTLB	3/2/01 0:00	SF											<1	<8	<2	<2	34	<2	<10	
DAPTLB	6/28/01 0:00	D	1.7	45100	8	<0.44	<0.05	0.37	0.0612		. 25	<10				•				

STATION	DATE/TIME	SAMPLES	Turb	EC	pН	NO3	NH3	TKN	PO4	oP	TSS	VSS	Cd	Cr	Cu	Pb	Ni	Ag	Zn	Hardness
		Type #	NTU	umhos		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	μ g/L	mg/L						
								Ŵ	est Basi	1										
DAPTWB	11/21/00 0:00	D	1.6	56300	8.1	<0.44	<0.05	0.94	<0.061		<10	<10								
DAPTWB	1/24/01 0:00	ST	3.9	47800	7.9	0.65	<0.05	0.62	<0.061		14	<10	<1	<8	<2	<2	16	. <2	23	
DAPTWB	1/24/01 0:00	SF											<1	<8	<2	<2	16	<2	18	
DAPTWB	1/26/01 0:00	ST	4.7	44600	8	0.47	<0.05	0.45	< 0.061		27	<10	<1	<8	3.1	<2	20	<2	24	
DAPTWB	1/26/01 0:00	SF											<1	. <8	<2	<2	19	<2	17	
DAPTWB	1/28/01 0:00	ST	1.9	55100	8.1	<0.44	<0.05	22	<0.061		36	<10	<1	<8	11	<2	23	<2	31	
DAPTWB	1/28/01 0:00	SF											<1	<8	<2	<2	23	<2	18	
DAPTWB	2/26/01 0:00	ST	11	32110	8.1	1.4	0.056	0.44	0.428		24	<10	<1	9.9	22	4.3	17	<2	43	
DAPTWB	2/26/01 0:00	SF											<1	<8	<2	<2	16	<2	12	
DAPTWB	2/28/01 0:00	ST	4.8	38710	· 8	0.83	<0.05	0.5	0.184		<10	<10	<1	8.7	<2	<2	38	<2	32	
DAPTWB	2/28/01 0:00	SF									· .		. <1	8.5	<2	<2	38	·<2	17	
DAPTWB	3/2/01 0:00	ST	1.7	46610	8.1	<0.44	<0.05	0.4	<0.061		13	<10	<1	8.5	<2	<2	33	<2	· 15	
DAPTWB	3/2/01 0:00	SF									•		<1	9.3	<2	<2	33	<2	14	· ·
DAPTWB	6/28/01 0:00	D	3.8	44320	8	<0.44	<0.05	0.38	0.0612		27	<10	•			•				

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STATION	DATE/TIME	SAMPLES	Turb	EC	pН	NO3	NH3	TKN	PO4	oP	TSS	VSS	Cd	Cr	Cu	Pb	Ni	Ag	Zn	Hardness
		Type #	NTU	umhos		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	μ g/L	μ <mark>g/L</mark>	μg/L	μ g/L	μ g/L	μ g/L	μ g/L	mg/L
							La	unch Ra	mp near	boatya	d									
DAPTLR	1/24/01 0:00	ST	2.3	50800	8	<0.44	<0.05	0.73	<0.061		<10	<10	<1	<8	<2	<2	.17	<2	15	
DAPTLR	1/24/01 0:00	SF			•								<1	<8	<2	<2	17	<2	. 12	
DAPTLR	1/26/01 0:00	ST	3.7	46100	8	0.48	0.08	0.38	<0.061		30	<10	<1	<8	<2	<2	20	<2	19	
DAPTLR	1/26/01 0:00	SF											<1	<8	<2	<2	22	<2	16	
DAPTLR	1/28/01 0:00	ST	2.2	54600	8.1	<0.44	<0.05	0.8	<0.061		<10	<10	<1	8.8	17	2.7	24	<2	36	
DAPTLR	1/28/01 0:00	SF											່ <1	<8>	<2	<2	24	<2	13	
DAPTLR	2/26/01 0:00	ST	7.8	36560	8.1	0,84	0.053	0.36	0.153		12	<10	<1	<8>	<2	<2	16	<2	15	
DAPTLR	2/26/01 0:00	SF											<1	<8	<2	<2	16	<2	<10	
DAPTLR	2/28/01 0:00	ST	3.2	45500	8	0.47	<0.05	0.47	0.0612		31	<10	<1	8	<2	<2	35	<2	15	
DAPTLR	2/28/01 0:00	SF											<1	<8	<2	<2	34	<2	13	
DAPTLR	3/2/01 0:00	ST	3.9	46410	8	<0.44	<0.05	0.45	<0.061		30	<10	· <1	9,1	<2	<2	36	<2	11	
DAPTLR	3/2/01 0:00	SF											<1	9,4	<2	<2	- 36	<2	12	

Appendix L-7

From P. Kozelka email from B. Ott 12/18/c

he: Wolf Labs = Cu For Dan Pt. Mari

Waterbod y	Collection dates	Org.	n	Min	Max	Mean	Median
San	199600	OCPFRD	91	2.1	100	16.4 ± 14	14.0
Diego	199799	IRWD	32	1.7	35.8	13.0	12.8
Creek	2000	Lee et al.	4	2.4	5.5	3.6	3.6
Santa	199600	OCPFRD	105	9.3	74	21.7 ± 4.4	18.1
Ana Delhi	2000	Lee et al.	3	5.0	6.3	6.4	6.3
Upper	199600	OCPFRD	83	3.4	29.0	11.0	11.0
Bay	1997—99	IRWD	10	1.2	2.3	1.7	1.7
Lower	199600	OCPFRD	25	8.2	26.3	15.9	16.1
Bay	199799	IRWD	6	0.6	3.4	2.3	2.3

Waterbod	Collection	Org.	n	Min	Max	Mean	Median
У	dates	-					
San	91-99	OCPFRD	172	0.2	53.0	8.5	4.4
Diego	97-98	IRWD	2	1.0	2.5		
Creek		·					
Upper	91-99	OCPFRD	66	3.0	190.0	23.6	17.0
Bay	94 & 96	BPTCP	7	5.8	40.80	26.91	35.40
	00-01	SCCWRP	10	11	58	30.9	25.5
Lower	91-99	OCPFRD	20	5.0	49.0	25.8	29.5
Bay	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
porewate	98	BIGHT	9	1.53	65.6	13.03	6.63
r		·		_ug/L	ug/L	ug/L	ug/L
Rhine	91-99	OCPFRD	18	29	530	316.5	330
Channel	94 & 96	BPTCP	2	479	505		
	00	Coastkeeper	2	170	270		
	00-01	SCCWRP	2	607	634		

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Waterbo dy	Collection dates	Org.	n	Min	Max	Mean	Median
San	1996-00	OCPFRD	96	1.0	70	4.4 ± 10.2	2.0
Diego	1997-99	IRWD	26	0.01	5.1	1.01	0.18
Creek	2000	Lee et al.	4	0.05	0.35	0.19	0.11
Santa	1996-00	OCPFRD	96	1.0	45	4.4 ± 6.1	2.0
Ana Delhi	2000	Lee et al.	3	0.03	0.95	0.63	0.90
Upper	199600	OCPFRD	83	<2	<20	3.1	2.0
Bay	1997—99	IRWD	10	0.023	0.96	0.44	0.29
Lower	199600	OCPFRD	25	<2	<2	<2	<2
Bay	1997—99	IRWD	6	0.03	0.89	0.45	0.43

Waterbod y	Collection dates	Org.	n	Min	Max	Mean	Median
San	91-99	OCPFRD	172	0.8	330	11.3	6.6
Diego Creek	97-98	IRWD	2	<10			
Upper	91-99	OCPFRD	66	3.3	47	16.8	12.8
Bay	94 & 96	BPTCP	7	14.2	29.6	20.1	20.4
	00-01	SCCWRP	10	7	37	18.6	17.5
Lower	91-99	OCPFRD	20	5.0	36	18.5	18.1
Bay	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
porewate r	98	BIGHT	9	0.32 ug/L	5.13 ug/L	0.95 ug/L	0.52 ug/L
Rhine	91-99	OCPFRD	18	26	140	78.5	87.5
Channel	94 & 96	BPTCP	2	78.1	95		
	00	Coastkeeper	2.	28	58		
	00-01	SCCWRP	2	72	87		

Waterbod y	Collection dates	Org.	n	Min	Max	Mean	Median
San	1996-00	OCPFRD	88	5.2	640	44.5 ± 80.0	16.5
Diego	199799	IRWD	38	3.5	106	13.0	12.0
Creek	2000	Lee et al.	4	2.6	23.1	13.1	8.2
Santa	1996-00	OCPFRD	105	10.0	532	93.7 ± 103.4	57.4
Ana Delhi	2000	Lee et al.	3	5.4	35.9	31.8	27.7
Upper	199600	OCPFRD	83	10	100	19.9	14.5
Bay	1997—99	IRWD	23	2.5	11.5	6.8	5.5
Lower	199600	OCPFRD	25	8.2	29.5	17.3 ± 6.2	16.3
Bay	1997	IRWD	13	1.1	44.4	8.6	7.5

Table ZZa	: Zinc Sedim	ent monitorin	g resu	lts by wate	rbody (mg	/ dry kg)	
Waterbod	Collection	Org.	n ·	Min	Max	Mean	Median
у	dates						
San	91-99	OCPFRD	173	1.0	200	36.2	22.5
Diego	97-98	IRWD	2	7.4	12	···· .	
Creek							
Upper	91-99	OCPFRD	66	4.2	210	79.4	67.2
Bay	94 & 96	BPTCP	7	46.4	171.0	115.3	136.0
	00-01	SCCWRP	10	48	169	115	108.5
Lower	91-99	OCPFRD	20	18.0	130.0	82.3	73.5
Bay	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
porewate r	98	BIGHT	9	3.85 ug/L	10.9 ug/L	6.06 ug/L	6.11 ug/L
Rhine	91-99	OCPFRD	18	86	340	198	195
Channel	94 & 96	BPTCP	2	236	303		
	00	Coastkeeper	2	77	120		
	00-01	SCCWRP	2	288	366		<u></u>

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Waterbod y	Collection dates	Org.	n	Min	Max	Mean	Median
San	1996-00	OCPFRD	73	0.5	18	1.7 ± 2.7	1.0
Diego	1997—99	IRWD	32	0.13	· 0.65	0.31	0.30
Creek	2000	Lee et al.	4	0.13	0.27	0.22	0.20
Santa	199600	OCPFRD	88	10.0	532	93.7 ± 103.4	57.4
Ana Delhi	2000	Lee et al.	3	0.08	0.14	0.12	0.10
Upper	199600	OCPFRD	83	<1	<10	1.6 ± 2.2	1.0
Bay	1997-99	IRWD	10	0.095	0.22	0.14	0.13
Lower	1996-00	OCPFRD	25	8.2	29.5	17.3 ± 6.2	16.3
Bay	199799	IRWD	6	0.084	0.23	0.17	0.17

Table ZZa	: Cadmium S	ediment mon	itorin	g results by	waterbody	y (mg/dr	y kg)
Waterbod	Collection	Org.	n	Min	Max	Mean	Median
у	dates					<u> </u>	
San	91-99	OCPFRD	173	1.0	200	36.2	22.5
Diego Creek	97-98	IRWD	2	7.4	12		
Upper	91-99	OCPFRD	66 ·	4.2	210	79.4	67.2
Bay	94 & 96	BPTCP	7	46.4	171.0	115.3	136.0
	00-01	SCCWRP	10	48	169	115	108.5
Lower	91-99	OCPFRD	20	18.0	130.0	82.3	73.5
Bay	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
porewate r	98	BIGHT	9	3.85 ug/L	10.9 ug/L	6.06 ug/L	6.11 ug/L
Rhine	91-99	OCPFRD	18	86	340	198	195
Channel	94 & 96	BPTCP	2	236	303		
	00	Coastkeeper	2 ·	77	120		
	00-01	SCCWRP	2	288	366		

Table ZZ	a: Arsenic Sec	diment monito	1				
Waterbod		Org.	n	Min	Max	Mean	Media
y San	dates	IRWD	2	<10			
Diego	97-98	BPTCP	7	2.5	7.3	5.3	5.6
Creek	97-90	DITCI		2.0	7.5	0.0	5.0
Upper	91-99	SCCWRP	10	1	6	4.2	4.5
Bay	94 & 96	BPTCP	11	6.7	11.5	8.7	8.2
	00-01	BIGHT	11	3.6	12.4	8.5	9.1
Lower	91-99	OGDEN	12	3.2	20	8.6	6.8
Bay	94	SCCWRP	8	2	10	6.3	7
	98	BIGHT	9	?ug/L	?ug/L	ug/L	ug/
	99	BPTCP	2	17.4	24.8		
	00-01	Coastkeepe r	2	5.3	9.4		
porewate r	98	SCCWRP	2	9	12		
Rhine	91-99	OCPFRD	18	86	340	198	195
Channel	94 & 96	BPTCP	2	236	303		
	00	Coastkeeper	2	77	120		
[00-01	SCCWRP	2	288	366		

Wash State120.Donohue770ShellfishNewport Bay240Wash State101	$\begin{array}{c ccccc} 0.2 - 4.0 & 1.3 \\ 15 - 10.7 & 3.5 \\ 0.2 - 65 & 5.1 \\ 0.8 - 2.5 & 1.3 \\ 1.0 - 6.9 & 2.4 \\ 0.2 - 126 & 15.9 \end{array}$	5 0.9 1 2.1 3 1.3
Donohue770ShellfishNewport Bay240Wash State101	D.2 - 65 5.1 D.8 - 2.5 1.3 1.0 - 6.9 2.4	1 2.1 3 1.3
ShellfishNewport Bay240Wash State101	0.8 - 2.5 1.3 1.0 - 6.9 2.4	3 1.3
Wash State 10 1	1.0 - 6.9 2.4	
		4 2.2
Donohue 57 0	2 126 150	
	.2 - 120 15.	9 4.2
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From:	<kozelka.peter@epamail.epa.gov></kozelka.peter@epamail.epa.gov>
То:	Brennan Ott <otbre@rb9.swrcb.ca.gov></otbre@rb9.swrcb.ca.gov>
Date:	12/27/01 11:55AM
Subject:	Re: Dana Point Harbor Split Sample Data

Hello Brennan--

First, let me clarify. We don't have any split samples from Dana Point Harbor; however, we do have two split samples from Newport Bay--one freshwater and one seawater.

second. attached are split sample results from Newport Bay and OCPFRD results of EPA samples (standard reference materials from Nat'l Res. Council Canada).

(See attached file: OCPFRD split sample results_Dec01.xls)

Bottom line----there is ample evidence that OCPFRD contract lab cannot produce a reliable Cu result in seawater!

IRWD was smart enough to use their own lab to develop the method and then double check using inter-laboratory analyses to verify their method was generating decent results.

Call me once you get this email and open the file, then it will be easier to explain.

Peter Kozelka, Ph.D.

NEW PHONE (415) 972-3448

FAX # (415) 947-3537

Brennan Ott <otbre@rb9.swr To: Peter Kozelka/R9/USEPA/US@EPA cb.ca.gov> cc: Subject: Dana Point Harbor Split Sample Data 12/27/2001 10:55 AM

Hi Pete.

If you get a chance, could you send me your split sample data for dissolved copper from Dana Point Harbor in the next day or so. We need to get this issue finalized real quick here and that data would really help in making a solid case for not listing DP harbor. Do you also know what lab IRWD used for the data you sent me and the method they used to test for dissolved copper. Thanks.

Sample		ole A 🛛	A Sample B			ple C	Sample D			
	saltw	<i>r</i> ater	estu	arine	dil. est	tuarine	freshwater <2 ppt			
salinity	35		15	ppt	7	opt				
	actual	OCPFRD	actual	OCPFRD	actual	OCPFRD	actual	OCPFRD		
	result	report	result	report	result	report	result	report		
Aluminum (Al)	n/a						54	1		
Antimony (Sb)	n/a						0.23			
Arsenic (As)	1.09		1.36		0.62		0.68			
Beryllium (Be)	n/a		n/a	· · · · · · · · · · · · · · · · · · ·	n/a		0.005	1		
Cadmium (Cd)	0.03	<1.0	0.048	<1.0	0.002	<1.0	0.012	<1.0		
Chromium (Cr)	0.092	13.0	0.183	9:9	0.084	<8.0	0.33	<8.0		
Cobalt (Co)	0.041			×			0.033			
Copped (OU) C.S.	READED 78	这些《 名印刷》是			## 107/14 m	9.0				
Iron (Fe)	1.26		0.568				103			
Lead (Pb)	0.012	<2.0	0.009	<2.0	0.004	<2.0	0.086	<2.0		
Manganese (Mn)	2.51						3.4			
Mercury (Hg)	n/a		n/a		n/a		n/a			
Molybdenum (Mo	8.95						0.21			
Nickel (Ni)	0.386	25	1:23	14	0:57		0.67	<4.0		
Selenium (Se)	0.042						n/a			
Silver (Ag)	n/a	<2.0	0.003	<2.0	0.001	<2.0	n/a	<2.0		
Strontium (Sr)	n/a						26.3	1		
Vanadium (V)	n/a						0.32			
Zinc (Zh)X 224		 ≤ 10/01 ≤ 1 	01201201	Sec. <10.0	······································	SI00 SI		而已经回到了		

.

Sample A is CASS-3 = Coastal Atlantic nearshore seawater Sample B is SLEW-3 = San Francisco Bay estuarine water Sample C is diluted (46%) SLEW-3

Sample D is SLRS-4 = Riverine Water

RESULTS OF EPA PFRD TRACE SAMPLES

SAMPLE	SAMPLE	SAMPLE	DATE	Cd	Cr	Cu	Pb	Ni	Ag	Zn
SITE	I.D.	MATRIX	ANALYZED	mg/L						
				RL = 1.0	RL = 8.0	RL = 2.0	RL = 2.0	RL = 4.0	RL = 2,0	RL = 10.0
EPA -SAMPLE A	WR41447	sw	9/10/01	<1.0	13.0	<2.0	<2.0	25.0	<2.0	<10.0
EPA -SAMPLE B	WR41448	SW	9/10/01	<1.0	9.9	5.0	<2.0	14.0	<2.0	<10.0
EPA -SAMPLE C	WR41449	AQ	9/10/01	<1.0	<8.0	9.6	<2.0	8.0	<2.0	<10.0
EPA -SAMPLE D	WR41450	AQ	9/10/01	<1.0	<8.0	5.3	<2.0	<4.0	<2.0	<10.0
CMCG02-PFRD	WR41385	AQ	9/10/01	<1.0	<8.0	12.0	<2.0	<4.0	<2.0	21.0
-CMCG02-EPA	WŘ41385.	AQ	9/10/01	10.100	2.000	930.	0.800	5.20	<0:005	22:5
	WR41439	SW	9/10/01	<1.0	16.0	4.9	<2.0	28.0	<2.0	19.0
UNBNSBEEPA	WR41439	SW SW	9/10/01	0.284	<0:005	3,44	0.123	1.25	<0:005	.9.2

LABORATORY: WECK

PREP: EPA 200.2

METHOD: EPA 200.8

DILUTION FACTOR: 1

SW = Sea Water

AQ = Fresh Water/Aqueous

EPA Region 9 Results (µg/L) for trace elements in two ambient water samples from OCPFRD. collected August 27 '01; analyzed Dec. 6, 2001

	Saltwater			Fresh Wa	ter					Reference	Seawater	
	WR41439		W	R14385 (CM	ICG02)		1		Non-	spike	Spike	Spike Dup
	North Star Bch			Filtered			MDL	Lab Blank			(% R	ecovery)
	result	<u>r1</u>	12	13	mean result	Stdev	(ug/L)	b1	r1	<u>r2</u>	ms1	ms2
Aluminum (Al)	44	18.5	15.3	15.1	16.3	1.56	0.005	nd	6.99	5.84	112	121
Antimony (Sb)	0.178	1.23	1.28	1.28	1.3	0.02	0.005	nd	0.124	0.11	47	51
Arsenic (As)	1.27	10.5	9.86	9,94	10.1	0128	0.01	ind -	the second	经代码	93 .	96
Beryllium (Be)	nd	nd	nd	nd	nd		0.005	nd	nd	nd	81	83
Cadmium (Cd)	0.284	0.11	0.103	0.095	0.10	0.01	0.005	nd	0.091	0.118	87	87
Chromium (Cr)	0.711	2.45	1.82	1.64	2.0	0.35	0.005	nd	0.223	0.294	98	100
Cobalt (Co)	nd	nd	nd	nd	nd		0.005	nd	nd	nd	.90	91
(Gulaialar (Cli))		LOTA .	0.00	SIG	215	0.97	COULT-			· +Tol Fires-	2)91	601
Iron (Fe)	14.9	131	117	111	119.7	8.38	0.005	nd	1.64	1.55	***	***
Lead (Pb)	0.123	0.85	0.795	0.758	0.80	0.04	0.005	nd	0.059	0.059	81	81
Manganese (Mn)	6.98	41.9	39.9	39.5	40.4	1.05	0.005	nd	0.582	0.728	90	89
Mercury (Hg)	nd With	ind 👷	nd	nd 👘	nd 🦾		0.005	nd	nd	nd	84	
Molybdenum (Mo)	11.7	5.09	4.93	5.05	5.0	0.07	0.005	nd	9.43	9.36	87	91
Nickel (Ni)	1.25	5.67	4.99	4.9	5.2	0.34	0.005	nd	0.493	0.497	86	87
Selenium (Se)	nd	nd	nd	nd	nd		0.01	nd	nd 🖉	nd	84	85
Silver (Ag)	nd	nd	nd	nd	nd		0.005	nd	nd	nd	78	82
Strontium (Sr)	36.5	781	794	796	790.3	6.65	0.005	nd	124	120	***	***
Thallium (TI)	nd	nd	nd	nd	nd		0.005	nd	nd	nd	86	90
Tin (Sn)	0.009	nd	nd	nd	nd		0.005	nd	nd	nd	89	94
Titanium (Ti)	0.731	1.19	1.01	1.07	1.1	0.07	0.005	nd	0.332	0.35	107	109
Vanadium (V)	2.12	7.67	6.92	6.83	7.1	0.38	0.005	nd	1.91	1.82	106	107
Zinc (Zh) ave shares	92	23.24	-22-15	22.2	22155	0.50	01005		2.12	28		

	DPS-01	DPS-02	DPS-03	DPS-04	DPS-05	DPS-06	REF-DPS-01	REF-DPS-02	REF-DPS-03	IS-DPS-01
Sampling	Copper									
Date	(mg/kg) dry									
26-Oct-92	13.8	12	16	10.1	5.6	18.1	3.8	5.6	-	10.4
27-Jul-93	23	19	19	- 15	19	37	5.1	6.6	- 2	12
3-Dec-93	99	39	54	30	35	82	12	22	-	33
4-Aug-94	138	67	96	55	41	175	18	29	30	49
12-Jul-00	768	573	573	-	-	888	60.65	238.7	71.3	-
11-Jul-01	. 72		579	-	-	533	585	229	57	-
11-Jul-01	95	-	429	-	-	609	472	258	62	-
11-Jul-01	86		507	-	-	808	637	246	84	

NOAA Sediment Quality Guidelines (informal, non-regulatory guidelines for use in interpreting chemical data from analyses of sediments) Data assembled from studies performed throughout North America. Saltwater only.

ERL (Effects Range Low) = 34 ppm, dry wt.

Concentration below which adverse effects rarely occur.

10th percentile

ERM (Effects Range Median) = 270 ppm, dry wt.

Concentration above which effects frequently occur.

50th percentile

Summary

37 of 62 (60%) samples exceeded ERL 18 of 62 (29%) samples exceeded ERM

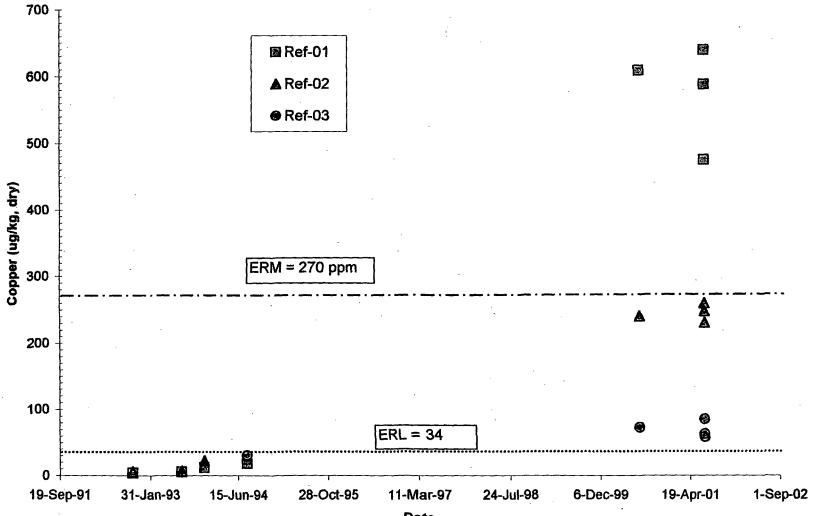
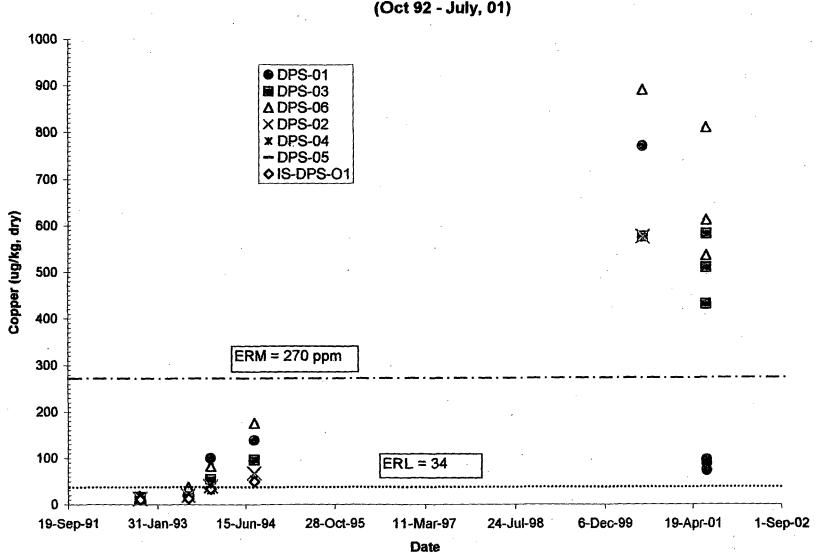
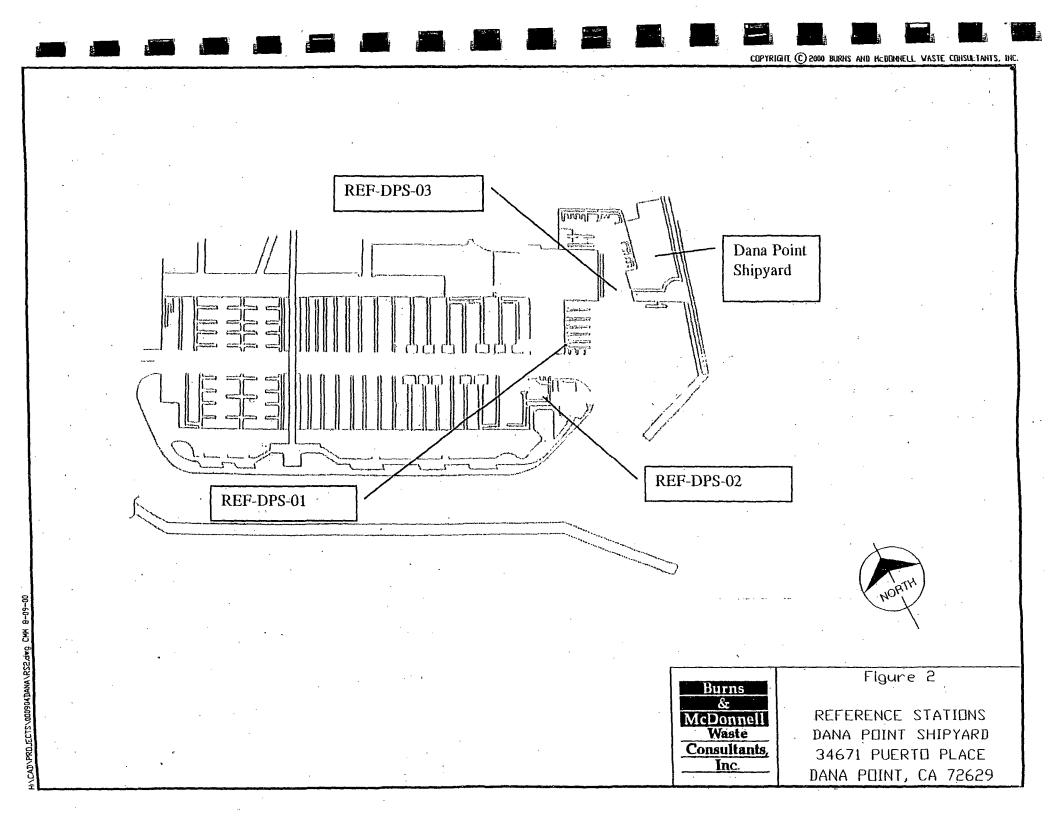


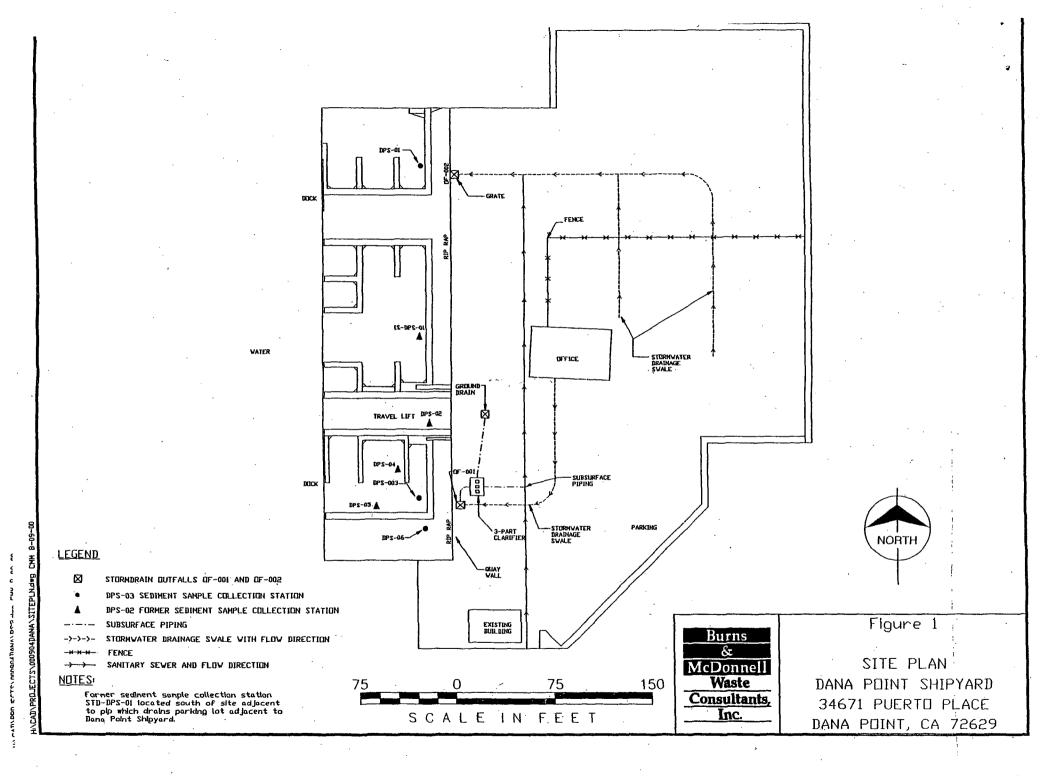
Figure 2: Copper in Dana Pt. Harbor Sediments - Reference Sites (Oct 92 - July, 01)

Date



Copper in Dana Pt. Harbor Sediments - Shipyard Sites (Oct 92 - July, 01)





Copper in Dana Point Harbor: To list or not to list?

4 January, 2002

Water Quality Criteria and Guidelines

The Criteria Maximum Concentration (CMC), 1 Hour Average for dissolved copper is 4.8 ug/L. The CMC is the California Toxics Rule water quality criteria to protect against acute effects in aquatic life and is the highest in stream concentration of a priority toxic pollutant consisting of a short-term average not be exceeded more than once every three years on the average.

The Criteria Continuous Concentration (CCC), 4 Day Average for dissolved copper is 3.1 ug/L. The CCC is the California Toxics Rule water quality criteria to protect against chronic effects in aquatic life and is the highest concentration of a 4-day average not to be exceeded more than once every three years on the average.

NOAA has published Sediment Quality Guidelines as informal, non-regulatory guidelines for use in interpreting chemical data from analyses of sediments. The ERL (Effects Range Low) is 34 ppm, dry wt. It is the lowest 10th percentile and is the concentration below which adverse effects rarely occur. The ERM (Effects Range Median) is 270 ppm, dry wt. It is the 50th percentile and is the concentration above which effects frequently occur.

EVIDENCE

Elevated dissolved copper

Data from the County of Orange's Annual NPDES Progress Report indicate elevated dissolved copper concentrations in Dana Point Harbor. Five stations were sampled within the harbor and just outside the mouth. Data goes as far back as 1991, but samples were not analyzed for dissolved copper until the year 2000. The permit requires only that two storm events be sampled per year. While there is some dry weather data, it was only analyzed for total copper. Therefore, all dissolved copper values come from storm events.

Dissolved copper data for three separate storm events has been reviewed (Table 1). Only the first storm event had concentrations above the applicable criteria. This occurred from 17 to 21 April 2000, when all 15 samples (3 at each of 5 sites) had concentrations above the CMC. The reported 4-day average for dissolved copper was above the CCC for all five stations. The CMC was exceeded by approximately 6 fold, while the CCC was exceeded by approximately 9 fold.

During the other two storm events, dissolved copper was only detected twice (detection limit of 2.0 μ g/L). These storms occurred from 24 to 28 January, 01 and from 26 February to 2 March, 01. The two detected values were 3.2 and 2.0 μ g/L and did not exceed the CCC. In total, 15 of 45 (33%) samples (3 of 9 at each station) exceeded the CCC (Table 1). Only 1 of 3 (33%) storms had elevated dissolved copper concentrations, but these values were well above the applicable criteria.

Lab QA / QC Concerns

Dr. Peter Kozelka of EPA Region 9 has raised concern over the validity of the data due to poor analytical technique by the contracted laboratory. The County of Orange has contracted the analysis of water column copper to Wek Laboratories. Wek Laboratories used ICPMS, EPA Method 200.8, a method commonly for the detection of dissolved copper in drinking water. Dr. Kozelka states that this test should not be used for dissolved copper in seawater because salt matrices are not removed from the water prior to analysis, which may result in a higher concentration than what is actually in the water. Phone conversations with Lab Managers at Wek Laboratories verified that salt matrices are not removed prior to testing. Dr. Kozelka has also submitted some data that demonstrates his concerns. A summary of inter-lab comparisons is reviewed (Table 2). Other summary data for several labs were also reviewed, but direct comparisons could not be made due to the difference in temporal span for which the mean and ranges were presented. Very few data points were presented that can be compared. Overall, Wek Laboratories was consistently above the EPA results. On average, they were higher by a factor of approximately 4.5 fold. If the 4-day average data from the first storm event were adjusted down by this factor, the concentrations would still exceed the CMC by about 4.5 times and the CCC by 1.5 times.

While Dr. Kozelka feels that there is "ample evidence that Wek Labs cannot produce a reliable Cu result in seawater," the evidence presented is not that compelling. Dave Smith of EPA Region 9 (Kozelka's Supervisor) believes that strong and conclusive evidence must be presented before a data set is disregarded. Dr. Kozelka understands this and is prepared to back us if we list or do not list dissolved copper in Dana Pt. Harbor.

Total Water Column Copper

Given the availability of total copper data, it is worthwhile to consider conversion of total copper data to dissolved copper concentrations. The USEPA Metals Translator¹ states a factor for conversion of saltwater 1-hour average total copper to dissolved copper concentrations of 0.83. This has been done for water column data for Dana Pt. Harbor beginning in October of 1997 (Table 3). When considering theoretical copper concentrations, all 5 stations exceeded the CMC of 4.8 μ g/L. In total, 32 of 36 (89%) samples exceeded the CMC (Figure 1). All 3-storm events had theoretical dissolved copper concentrations above the CMC.

Sediment Copper Concentrations

Sediment copper concentration data is available and help to understand the copper situation in Dana Point Harbor. Sediment copper is measured as total copper and has been collected by the Dana Point Shipyard. Wek Laboratories was not one of the laboratories that analyzed these sediment samples for copper. Sample locations exist within their facility and at three reference sites within the harbor. This discussion will be limited to the reference sites as they are considered more representative of general conditions within the harbor. Data is available for October 92 to August 94, July of 2000 and July of 2001 (Table 4). The earlier dates have much lower concentrations. They never exceed the ERM or the more stringent ERL criteria (Figure 2). The samples taken during 2000 and 2001 indicate that 12 of 12 samples exceeded the ERL and 4 of 12 (33%) exceeded the ERM (Figure 2). All exceedances of the ERM occurred at Station REF-01. For all samples and dates, 12 of 21(57%) samples exceeded the ERL and 4 of 21 (19%) exceeded the ERM.

Best Professional Judgement

Knowledge of the inherent nature of anti-fouling copper paints used on ship hulls is also considered as evidence. By their very design, these paints leach copper into the surrounding water as a means of controlling bio-fouling organisms. In an area of high boat densities, such as Dana Point Harbor, it is likely that the aquatic environment contains high dissolved copper concentrations. Perhaps for more than any other listing, this type of anecdotal evidence must be considered and weigh strongly in favor of 303(d) listing.

Conclusion

There is only limited direct evidence of elevated dissolved copper concentrations in Dana Point Harbor. One storm event resulted in all the direct evidence of exceedances. Furthermore, there is limited evidence that the data may not be valid due to analytical errors at the contracted laboratory. However, if the data is adjusted to account for the overestimates possibly attributable to the contracted lab, the concentrations for the one storm event still exceed the applicable criteria. These exceedances are also well above the criteria, indicating a high degree of impairment of beneficial uses during this rain event. Other water column data is also available for total copper. When these data are converted to dissolved copper concentrations, 2 stations now exceed the CMC during all 3-storm events and all 5 stations exceed the CMC during the first 2 storm events. In addition, total copper concentrations in the sediments are elevated above the ERM. Finally, the intrinsic nature of a marina filled with boats that are coated with copper based anti fouling paints provides additional evidence that Dana Point Harbor and its aquatic life beneficial uses are impaired due to elevated copper concentrations in the water column.

Reference

¹ Environmental Protection Agency, 1993. The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion. EPA 823-B-96-007.

Table 1: Copp	er, dissolved				
Station	DAPTEB	DAPTWB	DAPTLR	DAPTLB	DAPTHE
	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
17-Oct-97	7.6 DT	9.3 DT		5.2 DT	2 DT**
28-Oct-98		68.0 DT	63.0 DT	77.0 DT	
23-Jun-99		81.0 DT	117.0 DT	81.0 DT	
17-Apr-00		30.0 ST	38.0 ST	33.0 ST	33.0 ST
19-Apr-00		26.0 ST	22.0 ST	24.0 ST	22.0 ST
21-Apr-00	39.0 ST	37.0 ST	32.0 ST	35.0 ST	31.0 ST
24-Jan-01	3.5 ST	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
26-Jan-01	1.0 ST*	3.1 ST	1.0 ST*	2.4 ST	7.3 ST
28-Jan-01	8.7 ST	11.0 ST	17.0 ST	8.8 ST	1.0 ST*
26-Feb-01	8.1 ST	22.0 ST	1.0 ST*	1.0 ST*	1.0 ST*
28-Feb-01	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
2-Mar-01	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
17-Apr-00	27.0 SF	28.0 SF	26.0 SF	30.0 SF	21.0 SF
19-Apr-00		25.0 SF	21.0 SF	22.0 SF	20.0 SF
21-Apr-00		37.0 SF	35.0 SF	40.0 SF	30.0 SF
24-Jan-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
26-Jan-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	2.0 SF
28-Jan-01	3.2 SF	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
26-Feb-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
28-Feb-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
2-Mar-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
4-day avg					
17-21 Apr, 00	31.0 SF	30.0 SF	27.3_SF	29.0 SF	24.0 SF

* = Value reported as "<2.0"

** = Value reported as "<4.0"

ST (storm, total recoverable)

Avg =	13.4	14.7	12.7	11.9	10.9
Median =	8.1	11.0	1.0	2.4	1.0
Std Dev =	14.8	14.2	15.0	14.6	13.8
SF (storm, fil	tered)				
Avg =	11.2	10.7	9.8	10.9	8.7
Median =	1.0	1.0	1.0	1.0	1.0
Std Dev =	15.2	14.8	13.6	15.5	11.6

California Toxics Rule

Criteria Continuous Concentration (CCC), 4 Day Average (dissolved) = 3.1 ug/L CCC = the water quality criteria to protect against chronic effects in aquatic life and is the highest in stream concentration of a 4-day average not to be exceeded more than once every three years on the average.

Criteria Maximum Concentration (CMC), 1 Hour Average (dissolved) = 4.8 ug/L

CMC = the water quality criteria to protect against acute effects in aquatic life and is the highest in stream concentration of a priority toxic pollutant consisting of a short-term average not be exceeded more than once every three years on the average.

Summary

The CCC was exceeded during the period 17 - 21 April, 2000 The CMC was exceeded in 3 of 9 (33%) samples collected at each of the 5 sites (15 of 45 total) *All exceedances occured during storm events.*

Table 2: Interlab Comparison of Copper Concentrations

Sample ID	EPA Result Cu (mg/L)	Wek Result Cu_(mg/L)	Factor Above EPA
WR41385 (FW)	9.3	12	1.29
WR41439 (SW)	3.44	4.9	1.42
35 ppt salinity	0.517	<2.0	•
15 ppt salinity	1.55	5	3.23
7 ppt salinity	0.71	9.6	13.52
<2 ppt salinity	1.81	5.3	2.93
FW = fresh water		Avg above =	4.48
SM = opt water		-	

SW = salt water

 Table 3: Theoretical concentration of Dissolved Copper

Station		DAP	TEB	м. М	DAP	TWB		DAP	TLR		DAF	PTLB		DAF	PTHE
		(uç	ŋ/L)		(ug	ı∕L)		(ug	/L)		(นถุ	j/L)		(ug/L)	
Date	DT		Theoretical SF	DT		Theoretical SF	DT		Theoretical SF	DT	_	Theoretical SF	DT		Theoretical SF
17-Oct-97	7.6		6.3	9.3		7.7	-		er	5.2		4.3	-	-	-
28-Oct-98	57.0		47.3	68.0		56.4	63.0		52.3	77.0		63.9	-	-	-
23-Jun-99	96.0		79.7	81.0		67.2	117.0		97.1	81.0		67.2	-	-	
	ST	SF	Theoretical SF	ST	SF_	Theoretical SF	ST	SF	Theoretical SF	ST	SF	Theoretical SF	ST	SF	Theoretical SF
17-Apr-00	29.0	27.0	24.1	30.0	28.0	24.9	38.0	26.0	31.5	33.0	30.0	27.4	33.0	21.0	27.4
19-Apr-00	29.0	27.0	24.1	26.0	25.0	21.6	22.0	21.0	18.3	24.0	22.0	19.9	22.0	20.0	18.3
21-Apr-00	39.0	39.0	32.4	37.0	37.0	30.7	32.0	35.0	26.6	35.0	40.0	29.1	31.0	30.0	25.7
24-Jan-01	3.5	1.0*	2.9	1.0*	1.0*		1.0*	1.0*		1.0*	1.0*		1.0*	1.0*	
26-Jan-01	1.0*	1.0*		3.1	1.0*	2.6	1.0*	1.0*		2.4	1.0*	2.0	7.3	2.0	6.1
28-Jan-01	8.7	3.2	7.2	11.0	1.0*	9.1	17.0	1.0*	14.1	8.8	1.0*	7.3	1.0*	1.0*	
26-Feb-01	8.1	1.0*	6.7	22.0	1.0*	18.3	1.0*	1.0*		1.0*	1.0*		1.0*	1.0*	
28-Feb-01	1.0*	1.0*		1.0*	1.0*		1.0*	1.0*		1.0*	1.0*		1.0*	1.0*	
2-Mar-01	1.0*	1.0*		1.0*	1.0*		_1.0*	1.0*		1.0*	1.0*		1.0*	1.0*	

Theoretical SF = 83% of ST concentration

(US EPA 823-B-96-007 Metals Translator: to convert salt water 1 hr. avg total Cu to dissolved Cu multiply by 0.83)

Avg Theoretical Dsslvd Cu Std Deviation Total Theoretical Dissolved Std Deviation =	25.6 25.07 Cu =	26.5 22.06 28.0 23.79	40.0 31.01	27.6 25.52	19.4 9.72
Storm 1 (17-21 April, 00)					
Theoretical Avg SF=	26.8	25.7	25.5	25.5	23.8
Std Deviation =	4.79	4.62	6.71	4.86	4.86
Storm 2 (24-28 Jan, 01)		· · · · · ·			
Theoretical Avg SF=	7.2	5.9	14.1	4.6	6.1
Std Deviation =	-	4.64	-	-	
Strom 3 (26 Feb- 2 Mar, 01) Theoretical Avg SF= Std Deviation =	6.7	18.3	:	- -	

ST = Storm, total copper SF = Storm, dissolved copper

DT = Dry, total copper

Dana Pt. Shipyard Sediment Copper

:	DPS-01	DPS-02	DPS-03	DPS-04	DPS-05	DPS-06	REF-DPS-01	REF-DPS-02	REF-DPS-03	IS-DPS-01
Sampling	Copper	Copper	Copper							
Date	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry							
26-Oct-92	13.8	12	16	10.1	5.6	18.1	3.8	5.6	-	10.4
27-Jul-93	23	19	19	15	19	37	5.1	6.6	-	12
3-Dec-93	99	39	54	30	35	82	12	22	-	33
4-Aug-94	138	67	96	55	41	175	18	2 9	30	49
12-Jul-00	768	573	573	-	-	888	606.5	238.7	71.3	-
11-Jul-01	72		579	-	-	533	585	229	57	-
11-Jul-01	95	-	429	-	-	609	472	258	62	-
11-Jul-01	86		507		-	808	637	246	84	-

Table 4: Sediment Copper Concentrations in Dana Point Harbor

NOAA Sediment Quality Guidelines (informal, non-regulatory guidelines for use in interpreting chemical data from analyses of sediments) Data assembled from studies performed throughout North America. Saltwater only.

ERL (Effects Range Low) = 34 ppm, dry wt.

Concentration below which adverse effects rarely occur.

10th percentile

ERM (Effects Range Median) = 270 ppm, dry wt.

Concentration above which effects frequently occur.

50th percentile

Summary

37 of 62 (60%) samples exceeded ERL 18 of 62 (29%) samples exceeded ERM

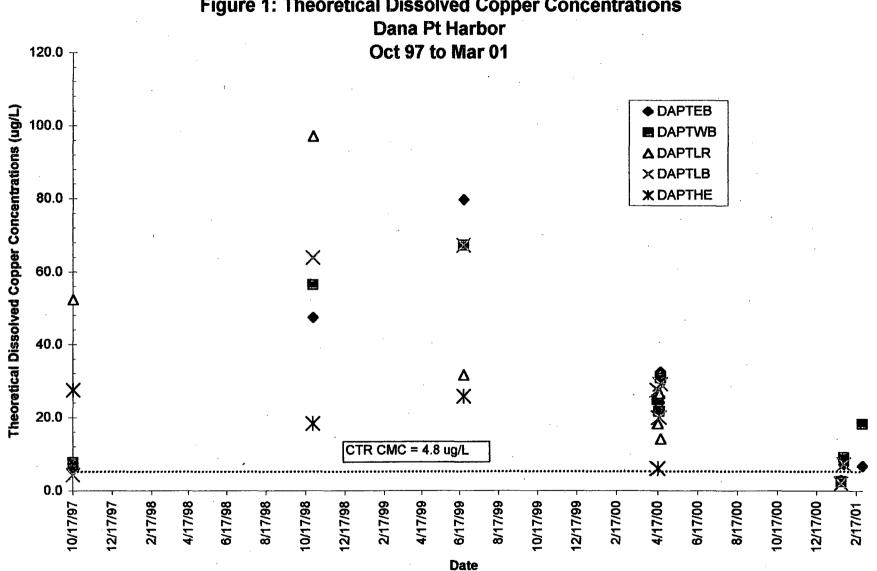


Figure 1: Theoretical Dissolved Copper Concentrations

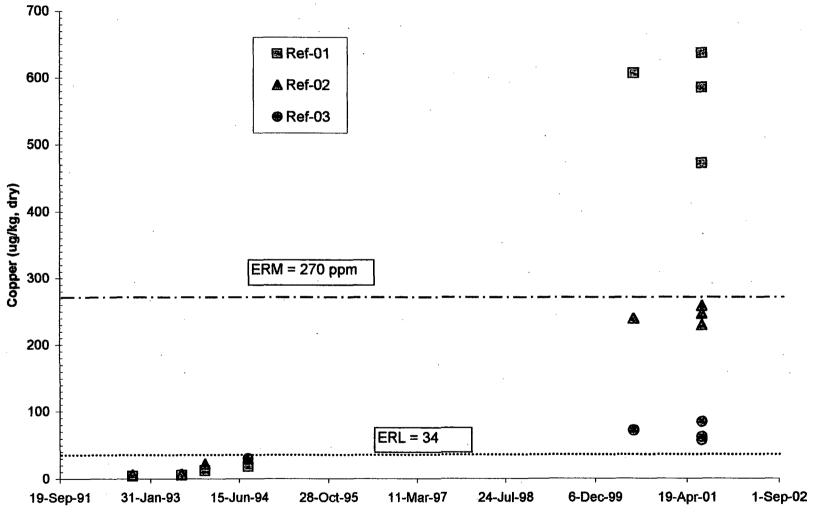


Figure 2: Copper in Dana Pt. Harbor Sediments - Reference Sites (Oct 92 - July, 01)

Date

-

Sediment Data from Subline 2 Jan 02

DANA POINT SHIPYARD

ERL = 34 ERM = 270

Station No. DPS-01		
Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92		13.8
7/27/93		23
12/3/93	36	99
8/4/94	55.2	
7/12/00	311	768
7/11/01	49	72
7/11/01	65	95
. 7/11/01	52	86

Station No. REF-DPS-01

Sampling Date	Copper (mg/kg) -Wet	
10/26/92		3.8
7/27/93		5.1
12/3/93	7	12
8/4/94	8	18
7/12/00	249.8	606.5
7/11/01	245	585
7/11/01	202	472
7/11/01	261	637

Station No. DPS-02

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92		12
7/27/93		19
12/3/93	19	39
8/4/94	. 21	67
7/12/00	224	573

Station No. DPS-03

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92		16
7/27/93		19
12/3/93	23	54
8/4/94	41	96
7/12/00		573
7/11/01	226	579
7/11/01	158	429
7/11/01	189	507

Station No. REF-DPS-02

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92	·	5.6
7/27/93		6.6
12/3/93	5	22
8/4/94	10	29
7/12/00	109	238.7
7/11/01	103	229
7/11/01	111	258
7/11/01	106	246

Station No. REF-DPS-03

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
8/4/94	12	30
7/12/00	39.3	71.3
7/11/01	36	57
7/11/01		62
7/11/01	49	84

Station No. DPS-04

Sampling Date Copper (mg/kg) -Wet Copper (mg/kg) -Dry

Station No. IS-DI	22-0	17	

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry

A Go 12my ð

10/26/92		10.1
7/27/93		15
12/3/93	12	30
8/4/94	28	55

Station No. DPS-05

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92		5.6
7/27/93		· 19
12/3/93	15	35
8/4/94	18	41

Station No. DPS-06

Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
10/26/92		18.1
7/27/93		37
12/3/93	34	82
8/4/94	80	175
7/12/00	334	888
7/11/01	230	533
7/11/01	278	609
7/11/01	346	808

 10/26/92
 10.4

 7/27/93
 12

 12/3/93
 11

 8/4/94
 15

Dana Poine Harbor9-23 From P. Kozelka 26 Feb 02

DANA POINT HARBOR Hydrologic Subarea 901.14

NEW 303(d) LISTINGS

Copper (dissolved) and Bacterial Indicators (please see Fact Sheet entitled "PACIFIC OCEAN SHORELINE FOR THE SAN DIEGO REGION" on pages B-71 to B-75 for rationale pertaining to the Bacterial Indicators listing recommendation)

PREVIOUS 303(d) LISTINGS

None

WATERSHED CHARACTERISTICS

Dana Point Harbor is a 215-acre waterbody in the San Juan Hydrologic Unit. It is classified coastal water with the following beneficial uses: IND, NAV, REC1, REC2, COMM, WILD, RARE, MAR, MIGR, SPWN AND SHELL¹.

WATER QUALITY OBJECTIVES NOT ATTAINED

Copper (dissolved)

The Criteria Maximum Concentration (CMC) 1-Hour Average for dissolved copper is 4.8 μ g/L. The CMC is the California Toxics Rule² water quality criteria to protect against acute effects in aquatic life and is the highest short-term average concentration of a priority toxic pollutant not to be exceeded more than once every three years on the average.

The Criteria Continuous Concentration (CCC) 4-Day Average for dissolved copper is 3.1 μ g/L. The CCC is the California Toxics Rule² water quality criteria to protect against chronic effects in aquatic life and is the highest 4-day average concentration not to be exceeded more than once every three years on the average.

NOAA has published Sediment Quality Guidelines³ as informal, non-regulatory guidelines for use in interpreting chemical data from analyses of sediments. The ERL (Effects Range Low) for total copper is 34 ppm, dry weight. It is the lowest 10th percentile and is the concentration below which adverse effects rarely occur. The ERM (Effects Range Median) for total copper is 270 ppm, dry weight. It is the 50th percentile and is the concentration above which effects frequently occur.

EVIDENCE OF IMPAIRMENT

Elevated Dissolved Copper

Data from the County of Orange's Annual NPDES Progress Report⁴ indicate elevated dissolved copper concentrations in Dana Point Harbor. Five stations were sampled within the harbor and just outside the mouth. Data goes as far back as 1991, but samples were not analyzed for dissolved copper until the year 2000. The permit requires only that two storm events be sampled per year. While there is some dry weather data, it was only analyzed for total copper. Only dissolved copper could be compared against the water quality objectives mentioned above. The Metals Translator⁵ was not used to convert total copper concentrations to dissolved copper concentrations due to the

Last updated 02/26/02 S:\WQS\303dlist\Fact Sheets-2002 listing\901 Page 1 of 5

uncertainty in the conversion during high flow events. Therefore, all dissolved copper values come from storm events.

Dissolved copper data for three separate storm events has been reviewed (Table 1). Only the first storm event had concentrations above the applicable criteria. This occurred from 17 to 21 April 2000, when all 15 samples (3 at each of 5 sites) had concentrations above the CMC. Pooling all 15 samples produced a mean of 28.5 μ g/L and a median of 27.0 μ g/L. This median concentration was over 460% above the CMC.

During the other two storm events, dissolved copper was only detected twice (detection limit of 2.0 μ g/L). These storms occurred from 24 to 28 January 2001 and from 26 February to 2 March 2001. The two detected values were 3.2 and 2.0 μ g/L and did not exceed the CMC. In total, 15 of 45 (33%) samples (3 of 9 at each station) exceeded the CMC (Table 1). Only 1 of 3 (33%) storms had elevated dissolved copper concentrations, but these values were well above the applicable criteria.

Table 1					
Station	DAPTEB	DAPTWB	DAPTLR	DAPTLB	DAPTHE
	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
17-0 ct-97	7.6 DT	9.3 DT	• •	5.2 DT	2 DT**
28-Oct-98	57.0 DT	68.0 DT	63.0 DT	77.0 DT	
23-Jun-99	96.0 DT	81.0 DT	117.0 DT	81.0 DT	
17-Apr-00	29.0 ST	30.0 ST	38.0 ST	33.0 ST	33.0 ST
19-Apr-00	29.0 ST	26.0 ST	22.0 ST	24.0 ST	22.0 ST
21-Apr-00	39.0 ST	37.0 ST	32.0 ST	35.0 ST	31.0 ST
24-Jan-01	3.5 ST	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
26-Jan-01	1.0 ST*	3.1 ST	1.0 ST*	2.4 ST	7.3 ST
28-Jan-01	8.7 ST	11.0 ST	17.0 ST	8.8 ST	1.0 ST*
26-Feb-01	8.1 ST	22.0 ST	1.0 ST*	1.0 ST*	1.0 ST*
28-Feb-01	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
2-Mar-01	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*	1.0 ST*
17-Apr-00	27.0 SF	28.0 SF	26.0 SF 3	30.0 SF	21.0 SF
19-Apr-00	27.0 SF	25.0 SF	21.0 SF	22.0 SF	20.0 SF
21-Apr-00		37.0 SF	35.0 SF	40.0 SF	30.0 SF
24-Jan-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
26-Jan-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	2.0 SF
28-Jan-01	3.2 SF	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
26-Feb-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
28-Føb-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*
2-Mar-01	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*	1.0 SF*

* = Value reported as "<2.0" DT = Dry, Total (total recoverable)

** = Value reported as "<4.0"

SF = Storm, Filtered (dissolved)

ST = Storm, Total (total recoverable)

Summary Statistics											
SF (storm, filtered)											
Avg =	11.2	10.7	9.8	10.9	8.7						
Avg = Median =	1.0	1.0	1.0	1.0	1.0						
Std Dev =	15.2	14.8	13.6	15.5	11.6						

Lab QA / QC Concerns

The County of Orange's contracted lab used EPA Method 200/8, an ICP/MS method commonly used for the detection of dissolved copper in drinking water. This method directs the analyst to correct for problems known to occur due to salt matrix interference. Phone conversations with lab managers at the contracted laboratory verified that salt matrices are not removed prior to testing. Therefore, it is likely that the data reported in Table 1 are incorrect.

EPA Region 9 has started an intercalibration study with several labs, including the County of Orange's contracted lab. The goal was to evaluate accuracy and recovery of metals within seawater and estuarine samples. The standard reference materials, which contain known concentrations of metals,

come from the National Research Council of Canada (NRCC). The NRCC and County of Orange's results for the same concentration of copper are presented in Table 2. Comparison of the results show the County of Orange's contracted lab to report much higher concentrations than the NRCC and provides evidence of the over estimation of dissolved copper when salt matrices are not removed. To date, limited data from this intercalibration study were reported and can be compared. While this preliminary quality assurance check suggests the contracted lab cannot produce a reliable dissolved copper result in seawater, the evidence presented is not so compelling that the data is considered invalid. Strong and conclusive evidence must be presented before a data set is disregarded. However, the data from the contracted lab must be viewed with caution.

Table 2: Split Sample Copper Concentrations	Table	Split Sa	mple Copper	Concentrations
---	-------	----------	-------------	-----------------------

Sample ID	NRCC* Cu (mg/L)	Orange Co. Result Cu (mg/L)
35 ppt salinity	0.517	<2.0
15 ppt salinity	1.55	5.0
7 ppt salinity	0.71	9.6
<2 ppt salinity	1.81	5.3

*NRCC = National Research Council Canada standard reference material

Sediment Copper Concentrations

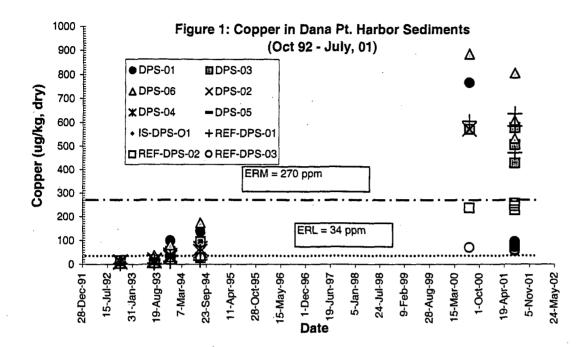
Sediment copper concentration data is available and helps in understanding the copper situation in Dana Point Harbor⁶. Sediment copper concentrations are not the basis for this listing decision, but add to the weight of evidence and confirm that copper is present in the harbor at levels sufficient to accumulate in sediment. Sediment copper is measured as total copper and has been collected by the Dana Point Shipyard. The laboratory contracted by Orange Co. was not one of the laboratories that analyzed these sediment samples for copper. Sample locations exist adjacent to the shipyard and at three reference sites within the harbor. Data is available for October 1992 to August 1994, July of 2000 and July of 2001 (Table 3). The earlier dates have much lower concentrations that occasionally exceed the ERM, but never exceed the more stringent ERL criteria (Figure 1). The samples taken during 2000 and 2001 indicate that 25 of 25 samples (100%) exceeded the ERL and 14 of 25 (56%) exceeded the ERM (Figure 2). For all samples and dates, SZ of 62 (60%) samples exceeded the ERL corrected SD-2002 and 18 of 62 (29%) exceeded the ERM. 63 $\chi \alpha$

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Table 3: Sediment Copper Concentrations in Dana Point Harbor

	Station									
· ·	DPS-01	DPS-02	DPS-03	DPS-04	DPS-05	DPS-06	REF-DPS-01	REF-DPS-02	REF-DPS-03	IS-DPS-01
	Copper	Copper	Copper	Copper						
Sampling	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)				(mg/kg)
Date	dry	dry	dry	dry	dry	dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	dry
26-Oct-92	13.8	12	16	10.1	5.6	18.1	3.8	5.6	•	10.4
27-Jul-93	23	19	19	15	19	37	5.1	6.6	-	12
3-Dec-93	99	39	54	30	35	82	12	22	-	33
4-Aug-94	138	67	96	55	41	175	18	29	30	49
12-Jui-00	768	573	573	-	-	888	606.5	238.7	71.3	-
11-Jul-01	72	-	579	-	-	533	585	229	57	-
11-Jul-01	95	-	429	•	-	609	472	258	62	-
11-Jul-01	86	-	507	-	•	808	637	246	84	-

(-)=not sampled



Best Professional Judgement

Knowledge of the inherent nature of anti-fouling copper paints used on boat hulls is also considered evidence. By their very design, these paints leach copper into the surrounding water as a means of controlling bio-fouling organisms. In an area of high boat densities, such as Dana Point Harbor, it is likely that the aquatic environment contains high dissolved copper concentrations. Perhaps for more than any other listing, this type of anecdotal evidence must be considered and weigh strongly in favor of 303(d) listing.

Summary of Evidence of Impairment

Copper is a commonly used pesticide in anti-fouling paints used on ocean vessels. There is only limited direct evidence of elevated dissolved copper concentrations in Dana Point Harbor. One storm event resulted in all the direct evidence of exceedances and there is limited evidence that the data may not be valid due to analytical errors at the contracted laboratory. However, during the one storm event, 100% of the samples exceeded the CMC by a large margin. Considering all three-storm events, one-third of the samples exceeded the CMC. In addition, total copper concentrations are now above the ERM at over half the stations sampled and exceed the ERL at all the stations. Finally, the intrinsic nature of a marina filled with boats that are coated with copper based anti fouling paints provides additional evidence that Dana Point Harbor has a dissolved copper problem. All of these lines of evidence constitute the weight of evidence that leads to the conclusion that the aquatic life beneficial uses of Dana Point Harbor are likely to be impaired due to elevated copper concentrations in the water column.

All of the above violations are expected to impair the WILD, RARE, MAR, MIGR, SPWN and SHELL beneficial uses.

EXTENT OF IMPAIRMENT

Copper (dissolved) The 5 water column sampling stations are distributed through out the entire harbor, including the mouth. The sediment sampling stations are also distributed through out the harbor. Finally, ships coated with copper-based anti-fouling paints are docked through out the harbor. Therefore, the entire harbor is listed as impaired for dissolved copper.

POTENTIAL SOURCES

Copper (dissolved) The California Regional Water Quality Control Board, San Diego Region's Draft Copper TMDL (Total Maximum Daily Load)⁷ has identified recreational boats as the major source of copper contamination to marina waters in San Diego Bay. This ongoing TMDL addresses elevated concentrations of dissolved copper in the Shelter Island Yacht Basin portion of San Diego Bay. Urban runoff is also considered a potential source.

TMDL PRIORITY

Copper (dissolved) Low

INFORMATION SOURCES

Water Quality Objectives

- ¹ Water Quality Control Plan for the San Diego Basin (9), 1994. California Regional Water Quality Control Board, San Diego Region.
- ² California Toxics Rule (Federal Register, 40 CFR, Part 131, Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California), May, 2000. Environmental Protection Agency.
- ³ National Oceanic and Atmospheric Administration, 2000. Sediment Quality Guidelines. Office of Response and Restoration. http://response.restoration.noaa.gov/cpr/sediment/SQGs.html
- ⁵ Environmental Protection Agency, 1993. The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion. EPA 823-B-96-007.
- ⁷ California Regional Water Quality Control Board, San Diego Region, 2001. Draft Staff Report for Copper TMDL in Shelter Island Yacht Basin. December 2001.

Data Sources

- ⁴ NPDES Annual Progress Report, County of Orange. November, 2000. Orange County Board of Supervisors. California Regional Water Quality Control Board, San Diego Region: Order No. 96-03.
- ⁶ Burns and McDonnell Engineers, 2001. Annual Sediment Sampling Report for Dana Point Shipyard. Project Number 23879. San Diego, CA. In compliance with California Regional Water Quality Control Board, San Diego Region Order No. 2000-212.

From:	James Smith
То:	Craig J. Wilson; Tim Stevens
Date:	12/4/02 4:58PM
Subject:	a bit more info for dana pt

Gentlemen,

Only very preliminary data exists that compares Orange Counties Lab against a lab using the correct procedures. Therefore, it would be premature to quantify the error in the Orange Co data. However, we do know it to be an overestimate and we dont believe it is over a factor of 10 error.

Interestingly enough, Orange Co seems to no longer be sampling for dissolved metals in the water column of Dana Point (they continue to do so in other harbors). Also, their latest report only indicates semiannual monitoring and that they are no longer sampling storm events. Unfortunately, due to the vagaries of the current permit, this may be acceptable.

However, they are continuing to collect sediment copper data:

Station Date Cu (mg/kg) DAPTEB 11/18/01 107 DAPTEB 6/26/02 74.3	There pepert (vol lot 2, Sectron 11) does compare there results against NOAAS ERM, therefore it is assumed these values are reported as dry weight.
DAPTLB 11/8/01 76.4 DAPTLB 6/26/02 79.7	is assumed these values are reported as dry weight.
DAPTLR 11/18/01 75.3 DAPTLR 6/26/02 70.8	4 Dec 00
DAPTWB 11/18/01 108 DAPTWB 6/26/02 55.4	

All measurements exceed the Effects Range Low, but none exceed the Effects Range Median. This is not the same source of sediment data that is found in our Fact Sheet. I am still attempting to find out if the Dana Point Shipyard is still collecting sediment data and if further information is available yet.

I did find some State Mussel Watch Program (SMWP) data from 1997. Transplanted mussels were found to contain 8.90 ppm (wet weight) and 69.3 ppm (dry weight). This wet weight concentration does exceed the EDL 85 as established by the SWMP.

None of this information may be overly compelling in favor of 303(d) listing. Region 9 does feel that the bulk of evidence warrants listing and that the detailed investigation into the degree and extent of the problem will be conducted during the initial phases of TMDL development.

-jimmy

J. Smith Environmental Scientist California Regional Water Quality Control Board, San Diego Region 9174 Sky Park Court, Suite 100 San Diego, CA 92123 (858) 467-2732 FX (858) 571-6972 www.swrcb.ca.gov/rwqcb9

CC:

Deborah Jayne

,	Station									
	DPS-01	DPS-02	DPS-03		DPS-05	DPS-06		REF-DPS-02	REF-DPS-03	IS-DPS-01
	Copper	Copper	Copper	Copper	Copper	Copper	Copper	Copper	Copper	Copper
Sampling Date	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry	(mg/kg) dry
26-Oct-92	13.8	12	16	10.1	5.6	18.1	3.8	5.6	-	10.4
27-Jul-93	23	19	19	15	19	37	5.1	6.6	-	12
3-Dec-93	99	39	54	30	35	82	12	22	-	33
4-Aug-94	138	67	96	55	41	175	18	29	30	49
12-Jul-00	1			-	-		. Å 1	238.7	71.3	-
11-Jul-01	72	-		-	-			229	57	-
11-Jul-01	95	-	· · · · ·	-	-	° si J° ′	· · · · ·	258	62	-
11-Jul-01	86	-		-	-	1.1.1		246	84	-
20-Jun-02	1. A.	-		-	-		170	1917	89	-
20-Jun-02	12 	-	·: .:	-	-	الدارية	159		98	-
20-Jun-02		-		-	-		165	256	91	-

Table 3: Sediment Copper Concentrations in Dana Point Harbor

(-) = not sampled

NOAA Sediment Quality Guidelines (informal, non-regulatory guidelines for use in interpreting chemical data from analyses of sediments) Data assembled from studies performed throughout North

ERL (Effects Range Low) = 34 ppm, dry wt.

Concentration below which adverse effects rarely occur. 10th percentile

是你会承诺的特殊。你是不能在你的关系是你的情况,你不能

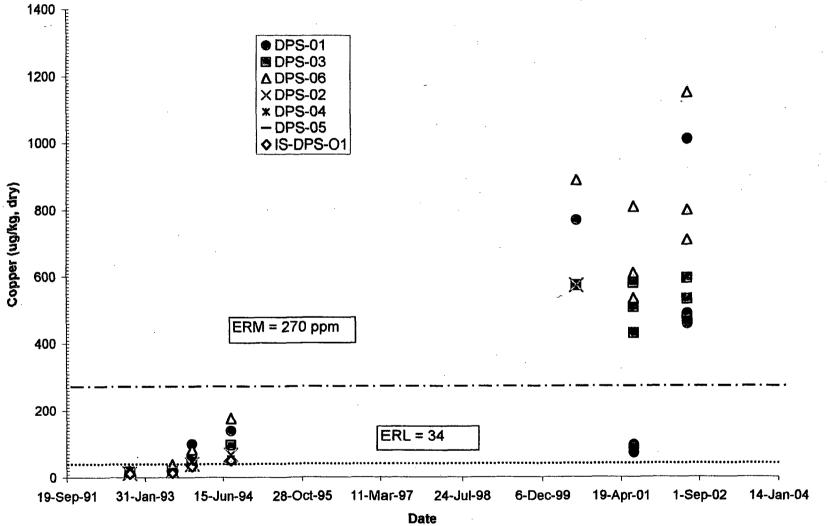
Concentration above which effects frequently occur. 50th percentile

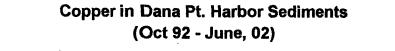
Summary (thru 11 July 01) 39 of 62 (63%) samples exceeded ERL 14 of 62 (23%) samples exceeded ERM

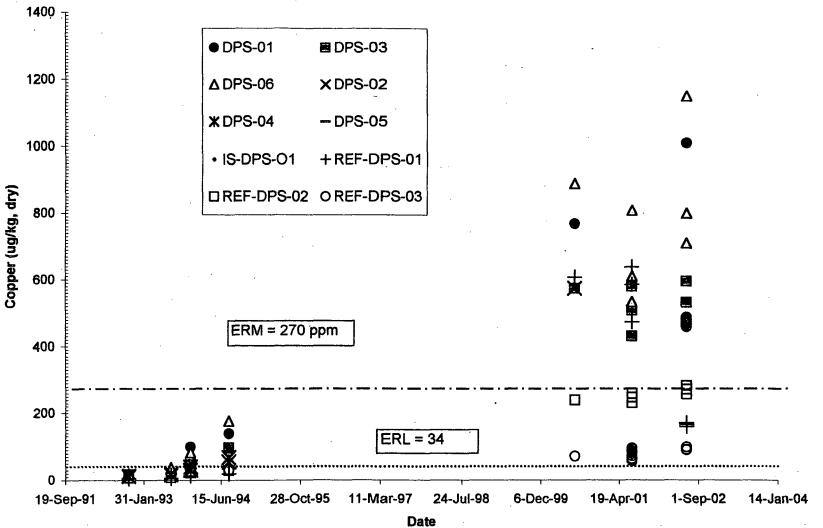
Summary (thru 20 June 02) 57 of 80 (71%) samples exceeded ERL 25 of 80 (31%) samples exceeded ERM

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Copper in Dana Pt. Harbor Sediments - Shipyard Sites (Oct 92 - June, 02)







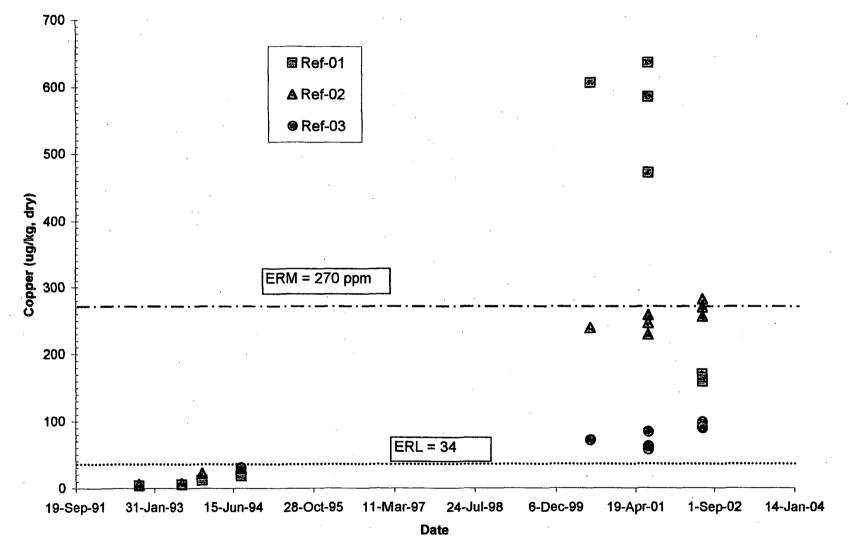


Figure 2: Copper in Dana Pt. Harbor Sediments - Reference Sites (Oct 92 - June, 02)

Thru 20 June 02

DANA POINT SHIPYARD

Station No. DPS-01

Rep #	Sampling Date		Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
	10/26/92			13.8	13.8
	7/27/93			23	23
	12/3/93	36	36	99	99
· ·	8/4/94	55.2	55.2	138	138
	7/12/00	311	311	768	768
1	7/11/01	49		72	
. 2	2 7/11/01	65		95	
	3 7/11/01	52	55	86	84
1	6/20/02	197	•	457	
2	2 6/20/02			1010	
3	6/20/02	199	266	487	651

Rep #

Station No. DPS-02

Rep #	Sampling Date	Cu (mg/kg) -wet mear	Cu(mg/kg) -dry mean
	10/26/92		12
	7/27/93		19
	12/3/93	19	39
	8/4/94	21	67
	7/12/00	224	573

Station No. DPS-03

Rep #	Sampling Date	Copper (mg/kg) -Wet	Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
	10/26/92			16	16
	7/27/93			19	19
	12/3/93	23	23	54	54
	8/4/94	41	41	96	96
	7/12/00	224	224	573	573
	1 7/11/01	226		579	
	2 7/11/01	158		429	
	3 7/11/01	189	191	507	505
	1 6/20/02	204		531	

Rep #	
	÷
	Π
	1
	231
	3
	2
	3



2	6/20/02	222		594	
3	6/20/02		203	470	532

Station No. DPS-04

Rep #	Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
	10/26/92		10.1
	7/27/93		15
	12/3/93	12	30
	8/4/94	28	55

Station No. DPS-05

Rep #	Sampling Date	Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
	10/26/92		5.6
	7/27/93		19
	12/3/93	15	35
	8/4/94	18	41

Station No. DPS-06

Rep #	Sampling Date	Copper (mg/kg) -Wet	Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
	10/26/92			18.1	18.1
	7/27/93			37	37
· .	12/3/93	34	34	82	82
	8/4/94	80	80	175	175
	7/12/00	334	334	888	888
	1 7/11/01	230		533	
	2 7/11/01	278		609	
	3 7/11/01	346	285	808	650
	1 6/20/02	291		709	-
	2 6/20/02	483		1150	
	3 6/20/02	316	363	799	886

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Rep	Rep #				

7/11/01	38		62	
7/11/01	49	41	84	68
6/20/02	51		89	
6/20/02	53		.98	1
6/20/02	50	51	91	93

Station No. IS-DPS-01

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Sampling Date		Copper (mg/kg) -Wet	Copper (mg/kg) -Dry
	10/26/92	-	 10.4
	7/27/93		12
	12/3/93	. 11	33
	8/4/94	15	 49
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Station No. REF-DPS-01

Sampling Date	Copper (mg/kg) -Wet	Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
10/26/92	2		3.8	3.8
7/27/9:	3		5.1	5.1
12/3/9	3 7	7	12	12
8/4/94	4 8	8	18	18
7/12/0	249.8	249.8	606.5	606.5
7/11/0	245		585	
7/11/0	202		472	
7/11/0	1 261	236	637	565
6/20/0	2		170	
6/20/02	2 75		159	
6/20/0	2 77	78	165	165

Station No. REF=DPS=02

Sampling Date	Copper (mg/kg) -Wet	Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
10/26/92			5.6	5.6
7/27/93			6.6	6.6
12/3/93	5	5	22	22
8/4/94	10	10	29	29
7/12/00	109	109	238.7	238.7
7/11/01	103		229	
7/11/01	111		258	
7/11/01	106	107	246	244
6/20/02	118		282	
6/20/02	117		270	
6/20/02	115	117	256	269

Station No. REF-DPS-03.

Sampling Date	Copper (mg/kg) -Wet	Cu-wet mean	Copper (mg/kg) -Dry	Cu-dry mean
8/4/9	12	12	30	30
7/12/0	39.3	39.3	71.3	71.3
7/11/0	36	· ·	57	