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WA-01-0050

DEPARTMENT OF ECOLOGY

October 14, 1993

TO: Lucy Pebles

FROM: Jim Cubbage

SUBJECT: Priority Pollutant Analyses of Sediments Within Maritime Contractors Shipyard in Bellingham Bay

BACKGROUND

This memorandum reviews results of sediment samples collected in March 1993 from three sites at the Maritime Contractors site in eastern Bellingham Bay. These samples were collected to survey the site for possible contamination from shipyard work.

METHODS

You and I took samples on March 30, 1993, following Puget Sound Protocols for sampling in marine sediments. Figure 1 shows the location of samples taken at Maritime Contractors in Bellingham Bay. We sampled from Ecology's 20 foot skiff equipped using a 0.1 m^2 stainless steel Van Veen grab sampler. Two subtidal sediment sites (Bell20 and Bell40) were located with a Magellan GPS (Global Positioning System) receiver as well as from sightings on nearby landmarks. The one site on shore (Bell41) was located at the end of a storm drain in the intertidal zone. Both subtidal sites had to be sampled several times before an adequate grab was recovered. A grab was considered adequate if it was filled with sediment and both the grab as well as access doors on top of the grab were closed tightly. For each grab, the top 2 cm of sediment not touching the walls of the grab was scooped out of the top doors of the sampler and placed in a stainless steel beaker. The intertidal sample was scooped directly into a beaker with a stainless steel spoon. The beaker contents were homogenized and subsamples for metals and organics (including PCB/pesticides and tributyltin) analysis were dispensed into separate 8 ounce priority pollutant-clean jars capped with teflon lid liners. Grain size samples were placed in Whirl-Paks®. Subsamples for total organic carbon analysis were placed in 4 oz jars. All stainless steel tools (beakers and spoons) were decontaminated prior to use with the following procedure: (washing in hot water and Liquinox® detergent, rinse in tap water, rinse in 10% nitric acid, rinse with deionized water, rinse with pesticide analysis grade acetone, air dry, and wrapped in aluminum foil. Between grabs, the sampler was thoroughly brushed and rinsed with on-site water.

Samples were analyzed for metals, grain size, percent moisture, total organic carbon, semivolatiles (base, neutral, and acids), chlorinated pesticides and PCBs, and butyltins. All

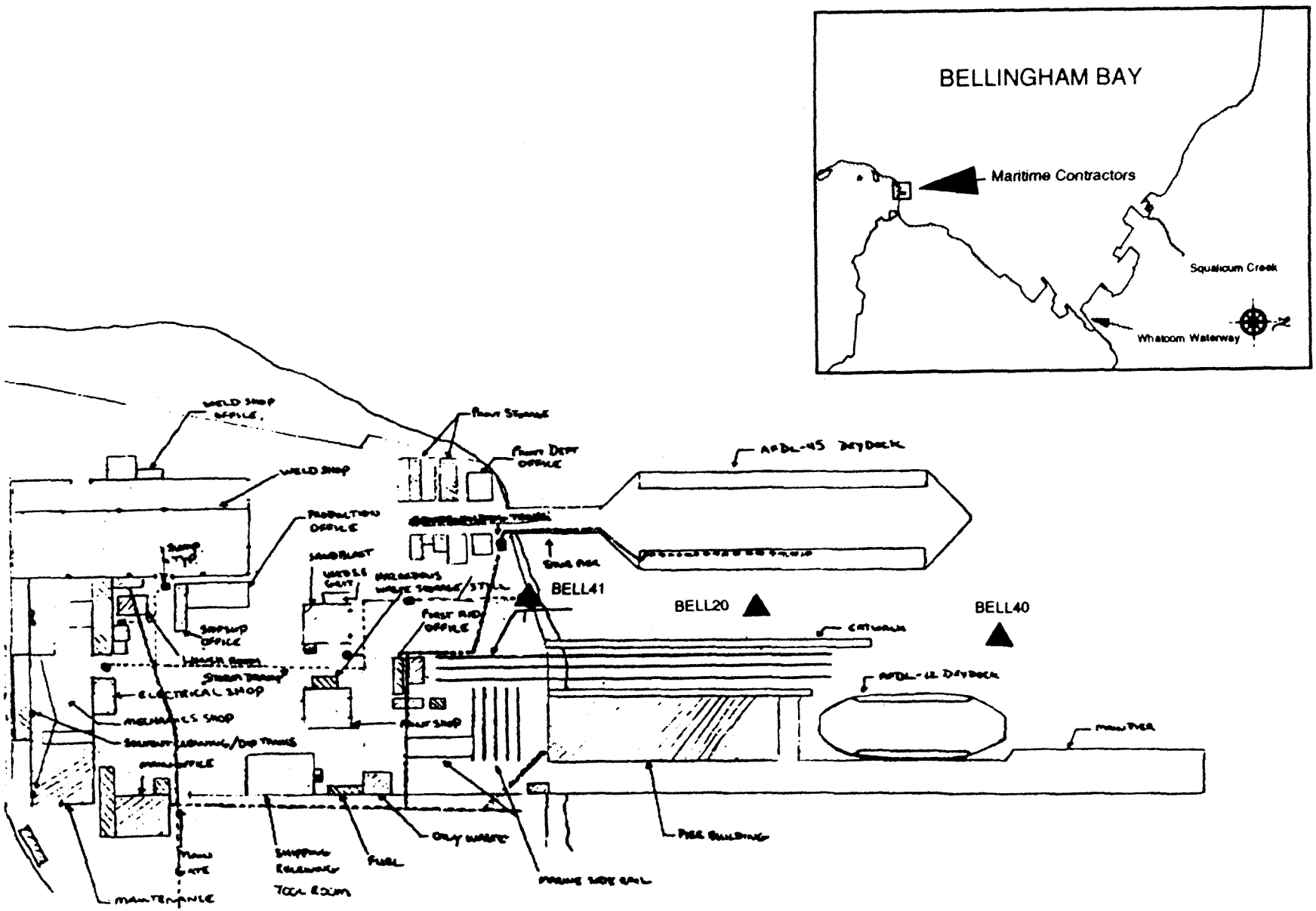

Figure 1. Map of Maritime Contractors and sample locations.

analyses were conducted within Puget Sound Protocols and EPA Contract Laboratory Program (CLP) procedures. Table 1 shows the analytical methods and laboratories. The laboratory case narrative for the analyses are attached and review aspects of quality control. Recoveries of metals spiked in samples run in the same analysis batch as these samples are shown in Table 2. All data can be used with the qualifications listed in the case narratives and in most cases the analyses were all within QA/QC guidelines. The exception is the butyltin analysis. Surrogate recoveries were unacceptably low and all results should be considered minimums.

RESULTS

Table 3 lists the results of metals analysis as well as Department of Ecology's Marine Sediment Quality Standards Chemical Criteria (WAC 173-204). Chemical values in sediments that fall below these criteria have no significant adverse effects on marine biological resources. Values above are considered to significantly affect biological resources. The shore site at the storm drain outfall exceeded criteria for arsenic, copper and zinc. The subtidal site farthest north exceeded criteria for copper and zinc. The other subtidal site exceeded criteria for lead only and was slightly (1.6%) above the lead criteria of 450 mg/kg. Higher concentrations of metals are often found in sediments with higher concentrations of fines (silt and clay). On the basis of percent fines alone, I would expect the outfall site to have the lowest concentrations of metals. However, the highest concentrations were found at the outfall, the site with the lowest fines (silt and clay), which suggests that the outfall may be a source for these metals in the sediments within the shipyard.

Table 4 shows concentrations of semivolatile organic compounds found at a minimum of one site and Table 5 summarizes detection limits of contaminants searched for, but not found. To allow comparisons to sediment criteria, concentrations in Table 4 have been normalized to total organic carbon concentrations. Only phenol exceeded criteria although dibenzofuran was close to the criteria at the mouth of the shipyard. Polycyclic aromatic hydrocarbons (PAH) were found at all three sites at concentrations below criteria. The two subtidal sites had equivalent values of PAH.

Table 6 reviews concentrations of chlorinated pesticides found in sediments at Maritime Contractors. PCBs were found at all three sites. Site 20 in the middle of the shipyard had the highest concentrations. Once normalized to total organic carbon, as shown in the bottom of the table, all three sites exceeded Marine Sediment Chemical Criteria (WAC 173-204) for total PCBs. PCBs, in the middle of the site (BELL20) exceed criteria by 250 fold and the next highest concentration is in the intertidal zone at the storm drain that drains the shipyard site. The presence of PCB at these levels at site BELL20 were confirmed with a separate GC-Mass Spec analysis. WAC 173-204 also provides cleanup criteria that specifies

Table 1. Analytical Methods.

Analysis	Method	Reference	Laboratory
Grain size	Seives and pipettes	EPA 1986a (PSEP protocols)	Soil Technology
% Moisture	Dry @ 105 degrees C	APHA 1985	EPA/Ecology Manchester
Total organic carbon	CO2/Combustion	EPA 1986a	ARI Laboratories
Arsenic	Atomic Absorption	EPA 1986b	EPA/Ecology Manchester
Cadmium	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Chromium	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Copper	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Mercury	Cold Vapor Atomic Absorption	EPA 1986b	EPA/Ecology Manchester
Lead	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Nickel	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Silver	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Zinc	Inductively Coupled Argon Plasma	EPA 1986b	EPA/Ecology Manchester
Semivolatiles (BNA)	GC/MS Method 8270	EPA 1986b	EPA/Ecology Manchester
Pest/PCB	GC/EC Method 8080	EPA 1986b	ARI Laboratories
VOAs	GC/MS Method 8240	EPA 1986b	EPA/Ecology Manchester
Organotins	TBT Method	Krone et al. 1989	EPA/Ecology Manchester

Table 2. Spike recovery results for metals and organotins.

	Lab No. 148165			Lab No. 148156		
	Spike Recovery			Spike Recovery		
	Result 1	Result 2	RPD*	Result 1	Result 2	RPD*
Arsenic	86%	86%	0%	88%	89%	1%
Cadmium	100%	97%	3%	103%	104%	1%
Chromium	82%	81%	1%	94%	92%	2%
Copper	98%	122%	22%	95%	93%	2%
Lead	81%	87%	7%	95%	93%	2%
Nickel	93%	94%	1%	96%	93%	3%
Silver	83%	88%	6%	18%	91%	134%
Zinc	94%	84%	11%	97%	96%	1%
	Lab No. 148166					
Mercury	103%	120%	15%			
	Lab No. 148172					
Tetrabutyltin	24%	20% U	-			
Tributyltin	51% J	21% J	83%			
Dibutyltin	18% U	20% U	-			

*RPD = Relative percent difference (a-b)/((a+b)/2)

U=No spike compound recovered at detection limit shown

J=Estimate due to low surrogate recoveries.

Table 3. Metals found in sediments collected at Maritime Contractors in Bellingham Bay (mg/kg dry wt.).

Site	Bell20 (Subtidal)		Bell40 (Subtidal)		Bell41 (Intertidal)		*Criteria**
Lab no	148167		148171		148172		*Ecology 1991*
Arsenic	15		55		78		*57*
Cadmium	1.2	P	1.8	P	1.6	P	*5.1*
Chromium	97		82		32		*260*
Copper	190		540		1400		*390*
Lead	460		90		220		*450*
Mercury	0.40		0.32		0.04	P	*0.41*
Nickel	160		130		94.8		*NC*
Silver	0.30	U	0.30	U	0.30	U	*6.1*
Zinc	260	E	900	E	1700	E	*410*
% Solids	60%		40%		80%		
%Gravel**	57%		1.0%		22%		
%Sand**	30%		36%		76%		
%Silt**	6.0%		29%		1.0%		
%Clay**	7.0%		34%		1.0%		

*Criteria = Washington State marine sediment quality standards.

Outline = exceeds Washington State marine sediment quality standards.

P=Metal detected above detection limit but below quantification limit.

U=Not detected at detection limit shown.

E=Concentration is estimate because of interference.

**Gravel=(>2000μm); Sand=(62.5μm-2000μm); Silt=(62μm-3.9μm); Clay=(<3.9μm)

NC=No criteria available

Table 4. Concentrations of semivolatile organic compounds found above detection limits in sediments Maritime Contractors in Bellingham Bay.

	µg/kg dry weight			mg/kg organic carbon			
	BELL20 (Subtidal) 148167	BELL40 (Subtidal) 148171	BELL41 (Intertidal) 148172	BELL20 (Subtidal) 148167	BELL40 (Subtidal) 148171	BELL41 (Intertidal) 148172	*Criteria** *Ecology, 1991*
BNA							
phenol	920	2400	400 U				*420* **
dibenzofuran	160 J	280 J	400 U	4 J	15 J		*15*
retene	130 J	220 J	400 U	4 J	12 J		
1-methylnapthalene	80 J	740 U	400 U	2 J			
2-methylnapthalene	71 J	90 J	400 U	2 J	5 J		*38*
napthalene	310 J	650 J	40 J	9 J	34 J	7 J	*99*
acenaphthylene	100 J	140 J	400 U	3 J	7 J		*66*
acenaphthene	160 J	110 J	25 J	4 J	6 J	4 J	*16*
fluorene	190 J	190 J	23 J	5 J	10 J	4 J	*23*
phenanthrene	1100	1180	400 U	31	62		*100*
anthracene	370 J	390 J	400 U	10 J	21 J		*220*
Sum LPAH	2400 J	2800 J	80 J	67 J	150 J	13 J	*370*
fluoranthene	1700	2200	400 U	47	110		*160*
pyrene	1900	1300 U	400 U	53			*1000*
benzo(a)anthracene	840	540 J	400 U	23	28 J		*110*
chrysene	1000	680 J	400 U	28	36 J		*110*
Benzo(a)pyrene	640 U	740 U	400 U				*99*
benzo(b)fluoranthene	920	690 J	400 U	26	36 J		*230*
ideno(1,2,3-cd)pyrene	480 U	740 U	400 U				
Dibenzo(a,h)anthracene	480 U	740 U	400 U				
Sum HPAH	6400	4100 J		180	210 J		*960*
Total Organic Carbon	3.60%	1.90%	0.61%				

*Criteria = Washington State marine sediment quality standards.

Outline = exceeds Washington State marine sediment quality standards.

U = Detection limit

J = Estimated concentration

** Phenol criteria measured in µg/kg dry weight

Table 5. Detection limits of semivolatile organic compounds not found in sediments from Maritime Contractors in Bellingham Bay. (μg/kg dry weight).

	BELL20		BELL40		BELL41	
	148167		148171		148172	
2,4-Dinitrophenol	9500	U	15000	U	8100	U
4-chloro-3-methylphenol	480	U	740	U	400	U
aniline	480	U	740	U	400	U
dimethyl nitrosamine	480	U	740	U	400	U
benzoic acid	560	U	740	U	400	U
hexachloroethane	480	U	740	U	400	U
hexachlorocyclopentadiene	4800	U	7400	U	4000	U
isophorone	480	U	740	U	400	U
diethylphthalate	480	U	740	U	400	U
di-n-butylphthalate	480	U	740	U	400	U
butylbenzylphthalate	480	U	740	U	400	U
n-nitrosodiphenylamine	480	U	740	U	400	U
carbazole	480	U	740	U	400	U
hexachlorobutadiene	480	U	740	U	400	U
pentachlorophenol	2400	U	3700	U	2000	U
2,4,6-trichlorophenol	480	U	740	U	400	U
2-nitroaniline	480	U	740	U	400	U
2-nitrophenol	1200	U	1900	U	1000	U
2-chloronapthalene	480	U	740	U	400	U
3,3'-dichlorobenzidine	950	U	1500	U	810	U
benzidine	950	U	1500	U	810	U
2-methylphenol	480	U	740	U	400	U
1,2-dichlorobenzene	480	U	740	U	400	U
chlorophenol	480	U	740	U	400	U
2,4,5 trichlorophenol	480	U	740	U	400	U
nitrobenzene	480	U	740	U	400	U
3-nitroaniline	480	U	740	U	400	U
4-nitroaniline	480	U	740	U	400	U
4-nitrophenol	1200	U	1900	U	1000	U
benzyl alcohol	480	U	740	U	400	U
4-bromophenyl-phenylether	480	U	740	U	400	U
2,4-dimethylphenol	480	U	740	U	400	U
4-methyphenol	480	U	850	U	400	U
1,4-dichlorobenzene	480	U	740	U	400	U
4-chloroaniline	480	U	740	U	400	U
pyridine	950	U	1500	U	430	U
bis(2-chloroethyl)ether	480	U	740	U	400	U
bis(2-chloroethoxy)methane	480	U	740	U	400	U
bis(2-ethylhexyl)phthalate	480	U	740	U	920	U
di-n-octyl phthalate	480	U	740	U	400	U
hexachlorobenzene	480	U	740	U	400	U
1,2,4-trichlorobenzene	480	U	740	U	400	U
2,4-dichlorophenol	480	U	740	U	400	U
2,4-dinitrotoluene	1200	U	1900	U	1000	U
dimethylphthalate	480	U	740	U	400	U
benzo(ghi)perylene	480	U	740	U	400	U
benzo(k)fluoranthene	480	U	740	U	400	U
4,6-dinitro-2-methylphenol	4800	U	7400	U	4000	U
1,3-dichlorobenzene	480	U	740	U	400	U
2,6-dinitrotoluene	1200	U	1900	U	1000	U
n-nitroso-di-n-propylamine	480	U	740	U	400	U
4-chlorophenyl-phenylene	480	U	740	U	400	U
1,2 diphenylhydrazine	950	U	1500	U	810	U
bis(2,chloroisopropyl)ether	480	U	740	U	400	U

Table 6. Chlorinated pesticides analysis of sediment samples taken near Maritime Contractors in Bellingham Bay. (μg/kg dry wt.)

	BELL20 (Subtidal) 148167	BELL40 (Subtidal) 148171	BELL41 (Intertidal) 148172
PESTICIDE			
alpha-BHC	1100 U	47 U	3.3 U
beta-BHC	1100 U	47 U	3.3 U
delta-BHC	1100 U	47 U	3.3 U
gamma-BHC	1100 U	47 U	3.3 U
heptachlor	1100 U	47 U	3.3 U
aldrin	1100 U	47 U	3.3 U
Heptachlor epoxide	1100 U	47 U	3.3 U
endosulfan I	1100 U	47 U	3.3 U
dieldrin	2200 U	95 U	6.6 U
4,4'-DDE	2200 U	95 U	6.6 U
endrin	2200 U	95 U	6.6 U
endosulfan II	2200 U	95 U	6.6 U
4,4'-DDD	2200 U	95 U	3.3 J
endosulfan sulfate	2200 U	95 U	6.6 U
4,4' -DDT	2200 U	95 U	6.6 U
methoxychlor	11000 U	480 U	33 U
endrin ketone	10000 U	95 U	6.6 U
endrin aldehyde	2200 U	95 U	6.6 U
gamma-Chlordane	1100 U	47 U	10 U
alpha-Chlordane	1100 U	47 U	3.3 U
toxaphene	110000 U	4800 U	330 U
PCB-1242/1016	22000 U	950 U	66 U
PCB-1248	80000 U	950 U	54 J
PCB-1254	61000	330 J	64 J
PCB-1260	30000 U	950 U	66 U
PCB-1221	44000 U	1900 U	140 U
PCB-1232	22000 U	950 U	66 U
PCB-1262	30000 U	950 U	66 U
PCB-1268	56000 J	950 U	290
Total PCBs	120000 J	330 J	410 J
Total organic carbon (OC)	3.6%	1.9%	0.6%
Total PCBs (mg/kg OC)	3300 J	18 J	67 J

Shade = found above detection limit.
U = detection limit
J = Estimated concentration
Outline = Exceeds Sediment criteria for PCBs (12 mg/kg OG)

maximum concentrations of chemicals that may remain 10 years after a cleanup action. This criteria for PCBs is 65 ppm organic carbon. Site Bell40 at the mouth is below this figure, site BELL41 near the storm drain is essentially at this figure (67 ppm organic carbon) and the subtidal site in the center of the shipyard exceeds this figure by 50 times.

The lower concentration found at the mouth of the shipyard suggests that PCBs in sediments may have come from the shipyard. However, the pattern does not mirror metals whereby the highest concentrations are found at the storm drain and suggests an upland source of contamination. DDD, a metabolite of DDT, was found in intertidal sediments at BELL41. No chemical criteria are listed for DDD.

Butlytin concentrations in sediments are shown in Table 7. Tributyltin (TBT) was found at all three sites at concentrations above the interim PSDDA screening level of 30 ppb. Sediments that exceed this interim level are required to be tested with bioassays to determine safe disposal options. TBT is used as an antifouling bottom paint so it is not surprising to find it at a shipyard. Other forms of butyltins were not found, but the quality assurance results showed the lab analysis probably would have missed other forms of butyltins if they were present. Indeed, the concentrations found here must be considered minimums because of several problems with the analysis that render these concentrations estimates (see Case Narrative for Butyltins).

SUMMARY

Table 8 reviews chemicals at sites that exceeded marine sediment criteria. All three sites exceeded at least three marine criteria. For metals, the highest concentrations were at the storm drain outlet in the intertidal area, the next highest was at the north opening of the shipyard (Bell40). The middle of the site had the most PCBs and these concentrations exceed both marine sediment chemical criteria and minimum cleanup standards criteria.

Table 8. Review of chemicals found in sediments at the Maritime Contractors Site.

Site	Chemicals above Marine Sediment Chemical Criteria (Ecology 1991)	Other chemicals
Bell20 - middle of shipyard (subtidal)	lead, phenol, PCBs	PAH, TBT,
Bell40 - Mouth of shipyard (subtidal)	copper, zinc, phenol, PCBs,	PAH, TBT Dibenzofuran
Bell41 - storm drain outfall from shipyard (intertidal)	arsenic, copper, zinc, PCBs	PAH, DDD, TBT

Table 7. Organotin found in sediments collected at Maritime Contractors in Bellingham Bay (μg/kg dry wt.).

Site	Bell20		Bell40		Bell41		*PSDDA* interim
Lab no	148167		148171		148172		*level**
Tetrabutyltin	20	U	40	U	20	U	
Tributyltin	282	J	392	J	173	J	*30*
Dibutyltin	20	U	40	U	20	U	

U=Not detected at detection limit shown.

J=Concentration is estimate because of poor surrogate spike recoveries.

*=Puget Sound Dredged Disposal Analysis interim screening level. If sediments exceed this level, biological tests are required to determine toxicity.

REFERENCES CITED

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JC:krc

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