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Quartermaster Harbor: Dockton;
A Reconnaissance Survey of Nearshore Sediments

by

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ABSTRACT

An abbreviated survey of sediments along the north-facing Dockton waterfront was conducted in hopes of shedding light on excessive herring egg-set mortalities in the area reported by the Washington State Department of Fisheries (WDF). Three sediment samples were analyzed for metals, one for acid/base/neutral priority pollutant organics, and numerous grab samples were visually inspected for discoloration/sheens indicative of significant PNA/oil/creosote contamination. No pollutants were identified at concentrations which would appear to make them likely causative agents for the elevated egg mortalities reported by WDF.

INTRODUCTION

The Washington State Department of Fisheries (WDF) has conducted herring spawning surveys since 1972. Since 1978, weekly visits to spawning sites have been conducted during the spawning season to estimate egg mortalities and spawning escapement (Penttila, 1986). Progress reports summarizing the findings of these surveys have been published annually (Gonyea, G., *et al.*, 1982a,b; Penttila, *et al.*, 1985). These reports document high mortalities in herring egg sets at certain locations in Puget Sound including Tulalip Bay, the east shore of Port Gamble, the south shore of Port Madison, and the Dockton shoreline of Quartermaster Harbor.

A memorandum from WDF to the Washington State Department of Ecology (Ecology) (Penttila, 1980) resulted in some initial work by the Biochemical Investigations Section of Ecology (Kittle, personal communication). This work was inconclusive.

Increasing concern about sediment contamination in Puget Sound and speculation that contamination of sediments in the Dockton area of Quartermaster Harbor might be responsible for unusual herring egg mortality in the area. Because herring eggs are typically laid on marine macroalgae and are not in contact with the sediments, a direct cause/effect relationship between sediment contamination and herring egg mortality would be difficult to establish.

Two classes of compounds were suggested as potential candidates for investigation; metals and polynuclear aromatic hydrocarbons (PNA's). Metals (particularly arsenic, copper, and lead) were suspected for two reasons: (1) the area is downwind of ASARCO copper smelter emissions,

and (2) the area was historically a site of some marine commerce (Palsson, personal communication) and certain heavy metals are associated with the anti-fouling paints used on boats. PNA's were suspected because there had been reports of hydrocarbon odors and slicks in the area, and the use of creosote in Puget Sound is widespread (pilings, etc.).

As noted earlier, direct cause/effect relationships between sediment contamination and herring egg mortality would be difficult to establish. However, the two classes of suspected compounds (metals and PNA's) tend to accumulate in sediments. Elevated sediment concentrations would be expected if there are sources in the vicinity which cause water column contamination.

A reconnaissance survey was conducted by the Toxics Investigations Unit of the Water Quality Investigations Section to address the issue of potential sediment contamination.

SURVEY DESCRIPTION

A reconnaissance survey was carried out on February 3, 1986. Art Johnson, Dale Norton, and Bill Yake of the Toxics Investigations Unit conducted the survey. Quartermaster Harbor and the study area are shown in Figure 1. Three nearshore (approximately 200 feet offshore) sediment samples were collected. All samples were analyzed for selected heavy metals, grain size, percent solids, and total organic carbon. The central site (B, Figure 1) was also analyzed for acid/base/neutral extractable priority pollutants (which include the PNA's).

Sediment samples were obtained with VanVeen and Ponar grabs cleaned with reagent-grade solvents, and acid-rinsed. The top 2 cm of sediment was removed, composited, and homogenized using stainless steel containers and spoons cleaned as above. Aliquots for separate analyses were obtained from the homogenate.

Organics, metals, and percent solids were analyzed at the Ecology/EPA laboratory at Manchester, Washington. Total organic carbon samples were sent out for analysis at Lauck's Testing Laboratories (Seattle), and the grain size samples for analysis at Parametrix, Inc. (Bellevue).

In addition to samples taken for analysis, numerous grabs of sediment were taken for visual observation. We were looking particularly for dark or oily sediment which might indicate PNA/creosote contamination. None was observed.

RESULTS AND DISCUSSION

The results of analyses of sediments collected during this survey are summarized in Table 1. This table summarizes results for compounds

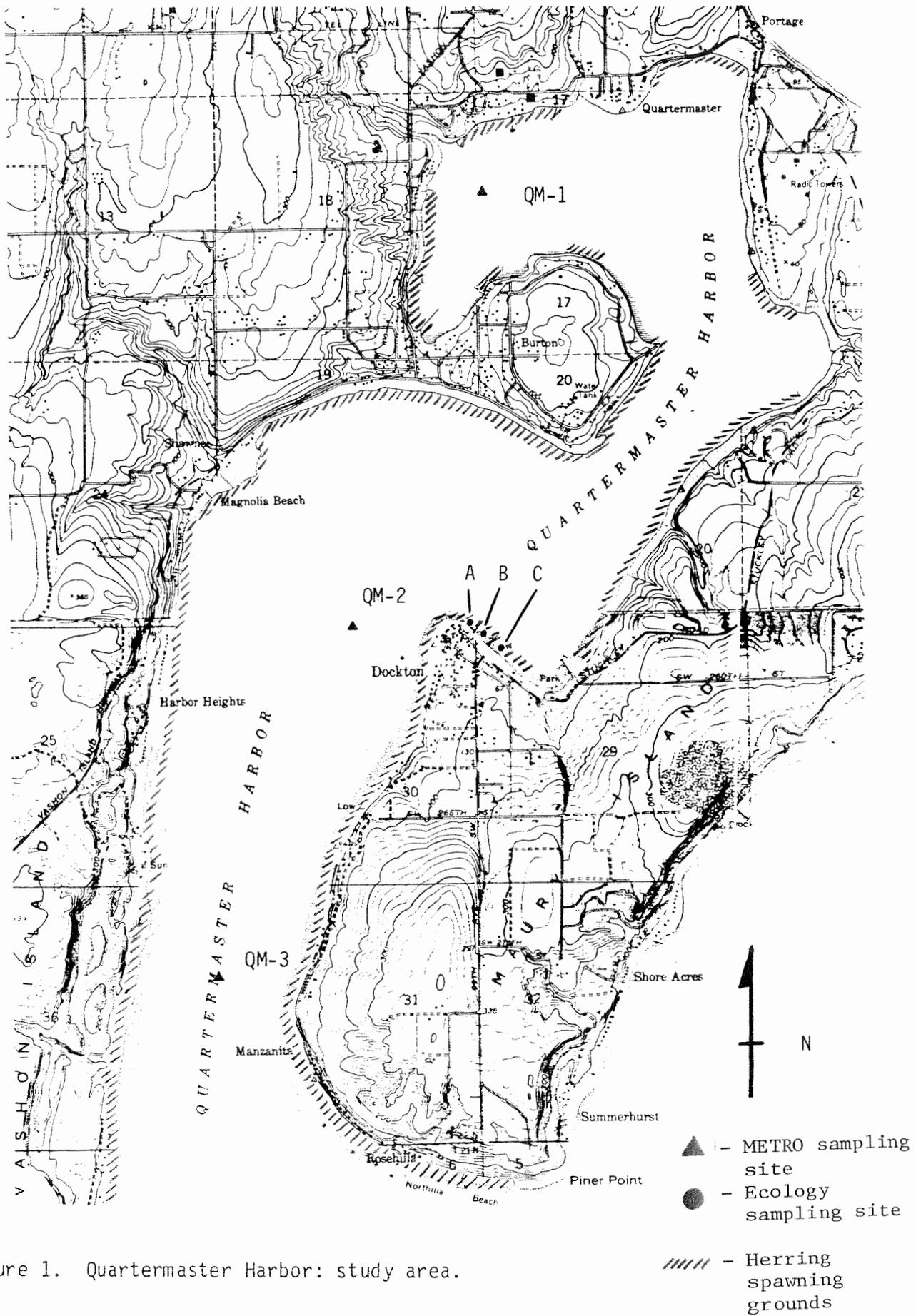


Figure 1. Quartermaster Harbor: study area.

Table 1. Results of sediment analyses.

Station	A	B	C
Sample Number	067312	067310	067311
Date Collected	2/3/86	2/3/86	2/3/86
Time	1440	1400	1425
Water Depth	13 ft.	18 ft.	16 ft.
<u>Metals (mg/Kg d.w.)</u>			
Arsenic	6.0*	5.5	8.5
Cadmium	0.54*	0.44	0.80
Chromium	17.0*	20.9	17.1
Copper	33.2*	34.6	29.8
Nickel	17.7*	28.1	20.2
Lead	29.6*	24.1	30.9
Zinc	34.4*	38.9	38.5
<u>Acid/Base/Neutral Extractable Organics (ug/Kg, d.w.)</u>			
Isophorone		7.3J	
Fluorene		13J	
Anthracene		30J	
Phenanthrene		75J	
Sum of low-weight PNA's		118J	
Fluoranthene		150	
Pyrene		190	
Chrysene		84J	
Benzo(a)anthracene		66J	
Benzo(b)fluoranthene		100J	
Benzo(k)fluoranthene		100J	
Sum of high-weight PNA's		590J	
Dibenzofuran		15J	
Di-n-octylphthalate		580	
Di-n-butylphthalate		240	
Diethylphthalate		20J	
Total Organic Carbon (percent)	0.9%	1.8%	1.5%
Percent Solids (metals aliquot)	69.2%	72.9%	66.2%
(organics aliquot)		69.4%	
Grain Size - Gravel (>2 mm)	0.82%	0.22%	14.98%
Sand (64 um - 2 mm)	81.74%	74.50%	70.56%
Silt (4 um - 64 um)	14.45%	21.08%	10.19%
Clay (< 4 um)	2.22%	1.38%	2.35%

* = Average of two replicate analyses

J = Estimated value

which were detected. Two additional compounds (N-nitrosodiphenylamine and bis [2-ethylhexyl]phthalate) were detected in Sediment B, but also were detected at similar concentrations in the blank, so are not reported. Full results including detection limits for compounds which were not detected are available on request.

Table 2 contains a summary of Quartermaster Harbor sediment data obtained from the Municipality of Metropolitan Seattle's (METRO's) Renton Baseline Study. Sampling site locations for both studies are shown in Figure 1.

Metals concentrations in Dockton area sediments were unexceptional and generally lower than those reported by METRO for QM1 (near head of harbor) and QM-2 (west of Dockton). Table 3 compares both present study results and METRO results to concentrations reported in reference areas (e.g., areas removed from obvious pollutant sources). In general, the Dockton area sediments have lower metals concentrations than median concentrations for those reference areas. The one exception to this generality is lead, which was approximately three times median reference area concentrations.

Table 3 also summarizes several sets of sediment values which presently serve as the best available "criteria" for judging the potential toxicity associated with pollutant concentrations in Puget Sound sediments. The values available for metals are called Apparent Effects Thresholds (AETs). Table 3 contains two types of AETs: one based on the results of bioassays using the marine amphipod Rhepoxinius, the other based on benthic infaunal community analysis. AETs are defined as the concentration above which significant biological effects are predicted to occur in sediments. Metals concentrations in Dockton area sediments are well below these AETs. Even lead which appears to be elevated with respect to reference areas, was present at concentrations of about 10 percent of the lower AET.

Several 3-ring (low-weight) and 4-, 5-, and 6-ring (high-weight) polynuclear aromatic hydrocarbons (PNA's) were detected in the single Dockton sediment sample analyzed for organics, as well as in METRO Quartermaster Harbor sediment samples.

The METRO data (despite being limited to three samples) imply a spatial trend for PNA's in Quartermaster Harbor with concentrations being highest near the head and lowest near the mouth. The Dockton waterfront sample taken during the present survey had PNA concentrations similar to the METRO sample (QM-2) to the west.

Based on comparisons in Table 3, METRO sample QM-3 near the mouth of Quartermaster Harbor is most similar in PNA concentrations to median reference area conditions. PNA concentrations of all three sediment samples obtained north of this site are somewhat elevated with respect to reference.

Table 2. Summary of METRO Quartermaster Harbor Sediment Data.

Station	QM-1	QM-2	QM-3
Date	7/82	7/82	2/84

Metals mg/Kg d.w.)

Arsenic	26.9	45.3	
Cadmium	1.314	0.287	
Chromium	83.5	78.5	
Copper	61.3	53.8	
Nickel	41.8	40.4	
Lead	57.1	43.5	
Zinc	94	87	

Acid/Base/Neutral Acid Extractables (ug/Kg d.w.)

Fluorene	1000m	13m	52m
Anthracene	30m	130m	3m
Phenanthrene	110	690	13m
Total low-weight PNA's	<u>1100m</u>	<u>830m</u>	<u>68m</u>
Fluoranthene	500	240	13m
Pyrene	530	240	26m
Chrysene	280m	160	ND
Benzo(a)anthracene	170m	120	ND
Benzo(b)fluoranthene	250	130	ND
Benzo(k)fluoranthene	170	91	ND
Benzo(a)pyrene	20m	ND	ND
Dibenzo(a,h)anthracene	190	80	ND
Indeno(1,2,3-cd)pyrene	220	84	ND
Benzo(g,h,i)perylene	<u>2300m</u>	<u>1150</u>	<u>39m</u>
Total high-weight PNA's	280	270	780
Di-n-octyl phthalate	ND	ND	6m
Diethyl phthalate	ND	4m	ND
Butylbenzyl phthalate			
Percent Solids	36%	45%	77%

m = Detected but less than quantification limit given (<).
 ND = Not detected.

Sources: Word, et al., 1984; Buffo, 1986.

Table 3. Quartermaster Harbor sediment concentrations compared to reference area and "criteria" values.

Study Station	Quartermaster Harbor Results						Comparison Values (Tetra Tech, 1986)			
	Present Study			METRO			Reference Area Medians ¹	Screening Level ²	Apparent Effects Thresholds	
	A	B	C	QM-1	QM-2	QM-3			Amphipod ³ Bioassay	Benthic Infauna ⁴
Metals (mg/Kg d.w.)										
Arsenic	6.0	5.5	8.5	26.9	45.3		5.6		93	85
Cadmium	0.54	0.44	0.80	1.314	0.287		0.7		6.7	5.8
Chromium	17.0	20.9	17.1	83.5	78.5		40		>130	59
Copper	33.2	34.6	29.8	61.3	53.8		33		800	310
Nickel	17.7	28.1	20.2	41.8	40.4		23		>120	49
Lead	29.6	24.1	30.9	57.1	43.5		9.6		700	300
Zinc	34.4	38.9	38.5	94	87		76		870	260
Acid/Base/Neutral Organics (ug/Kg d.w.)										
Fluorene		13J		1000m	13m	52m	2.5		540	640
Anthracene		30J		30m	130m	3m	6		960	1300
Phenanthrene		75J		110	690	13m	14	(351)	2100	3200
Total low-weight PNA's		118J		1100m	830m	68m	24		5200	6100
Fluoranthene		150		500	240	13m	24	(587)	3900	6300
Pyrene		190		530	240	26m	22	(533)	4300	>7300
Chrysene		84J		280m	160	N.D.	5.5	(365)	2800	6700
Benzo(a)anthracene		66J		170m	120	N.D.	10		1600	4500
Benzofluoranthenes		100J		250	130	N.D.	18		3700	8000
Benzo(a)pyrene		130u		170	91	N.D.	8.4	(554)	2400	6800
Dibenzo(a,h)anthracene		130u		20m	20m	N.D.	N.D.		260	1200
Indeno(1,2,3-cd)pyrene		130u		190	80	N.D.	6.6		690	>5200
Benzo(g,h,i)perylene		130u		220	84	N.D.	7.6		740	5400
Total high-weight PNA's		590J		2300m	1150	39m	76		18,000	>51,000
Dibenzofuran		15J					<5		540	540

J = Estimated value.

m = present at less than quantification limit given.

N.D. = Not detected; detection limit unknown.

¹Median concentration in Puget Sound sediments removed from anthropogenic influences.

²Previously termed "probable no-effect levels," based on benthic infaunal distributions.

NOTE: () = Converted from original values by using 1.4 percent total organic carbon.

³Concentrations above which increased mortality in amphipod bioassay has always been observed.

⁴Concentrations above which depletions in at least one taxon of benthic invertebrates has always been noted.

Included in Table 3 are "screening-level" concentrations. These were developed for USEPA and were originally termed "probable no-effects levels." They represent concentrations below which no adverse effects on benthic community structure have been measured. In many cases it is likely that the concentrations at which pollutants begin to have measurable adverse effects on benthic fauna is between the screening level and the AETs. The "screening level" values were originally expressed on a ug/Kg of total organic carbon basis. For Table 3, they have been converted to a dry-weight basis by multiplying by 1.4 percent (the mean total organic carbon concentration for the three Dockton waterfront samples). For all PNA's for which "screening-level" concentrations are available, the Dockton waterfront sediment is lower. The Dockton sediment sample PNA's are in all cases well below (at least one order of magnitude) the equivalent AET.

As noted earlier, a number of sediment grabs were brought to the surface for visual inspection. No discoloration typical of significant PNA/creosote contamination was observed. No slicks were observed in the study area.

Based on the available data, there is no evidence of notable PNA/creosote contamination in the Dockton waterfront area. Based on earlier METRO work, the head of the harbor may warrant further investigation.

Several other organics were detected in the Dockton waterfront sample: isophorone, dibenzofuran, and several phthalates. Isophorone has been detected rarely (if ever) in Puget Sound sediments. The EPA criteria document (EPA, 1980) notes that "Isophorone is an excellent solvent . . . but it is used mainly as a solvent for vinylic resins applied by roller coating." Based on its relatively low acute toxicity (the saltwater acute criterion for protection of saltwater aquatic life is 12,900 ug/L), it is unlikely that its presence in the Dockton sediments at low concentrations (estimated 7.3 ug/Kg d.w.) would have a measurable deleterious effect.

Dibenzofuran also was noted at a low (estimated 15 ug/Kg d.w.) level. The AET for dibenzofuran is about 35 times higher.

Phthalates are plasticizers which are commonly reported in sediment samples and have a relatively low toxicity. They have not been linked to adverse effects in Puget Sound.

CONCLUSIONS

Based on limited sampling along the Dockton waterfront, no pollutants were identified in sediments at concentrations which would appear to make them likely causative agents for the elevated herring egg-set mortalities reported by WDF.

Concentrations of six of seven metals (lead excluded) were at or below median reference area concentrations. Concentrations of all seven were well below AET concentrations at which adverse biological impacts are predicted.

A number of polynuclear aromatics were detected in the single sediment sample analyzed for acid/base/neutral priority pollutant organics. While concentrations for these PNA's appeared to be somewhat elevated with respect to reference areas, they were well below concentrations associated with negative biological effects. Based on analytical results and visual examination of a number of sediment samples in the area of concern, there is no evidence of notable PNA/creosote contamination in the Dockton waterfront area.

Several other organics were detected in the Dockton sediment, but none at concentrations high enough to indicate probable adverse effects on marine biota.

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